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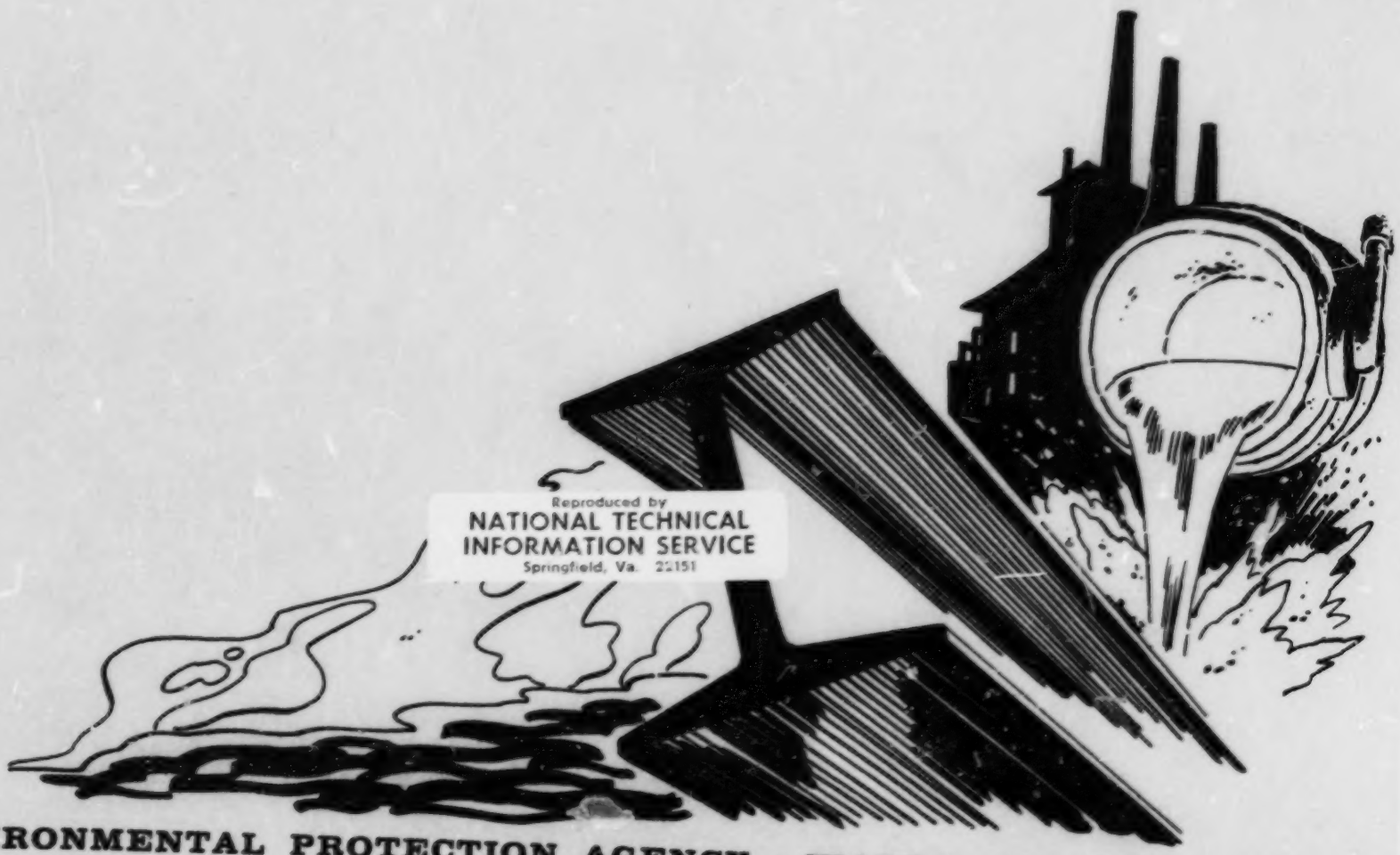
An Electromembrane Process for Regenerating Acid from Spent Pickle Liquor



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A method of removing iron from spent liquor that involves the formation of insoluble iron hydroxides is preferrable to plating iron metal onto cathodes.

Estimated treatment costs were $0.045 ± 0.002 per gallon, whereas the combined costs of purchasing acid and disposing of spent liquor by existing methods were in the range of $0.015 to $0.06 per gallon of spent liquor.

A determination of the long-term performance of the ion-exchange membranes when treating actual pickle liquors that contain organic pickling aids is needed.

This report was submitted in fulfillment of Project 12010 EQF under the partial sponsorship of the Water Quality Office.

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AN ELECTROMEMBRANE PROCESS FOR REGENERATING ACID FROM SPENT PICKLE LIQUOR

Submitted to

ENVIRONMENTAL PROTECTION AGENCY
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Studies of an electromembrane process for regenerating acid from spent sulfuric acid pickle liquor have indicated that the process is technically feasible. The studies have shown that the iron ions in spent pickle liquor can be removed and replaced by hydrogen ions to regenerate H_2SO_4 in electromembrane cells.

A method of removing iron from spent liquor that involves the formation of insoluble iron hydroxides is preferable to plating iron metal onto cathodes.

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Key Words: Industrial wastes, spent pickle liquor, pickling of steel, acid regeneration, ferrous sulfate, membrane processes, treatment costs, ion-exchange membranes, electrolytic cells.

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AN ELECTROMEMBRANE PROCESS FOR REGENERATING ACID FROM SPENT PICKLE LIQUOR

I. CONCLUSIONS

The main conclusions from this study are:

1. Either a batch-recycle or a continuous electromembrane acid-regeneration process appears to be technically feasible on the basis of the relatively short-term experiments performed so far. One of the major questions remaining is the long-term behavior of the membranes used in the process. (The longest term of service of any set of membranes, so far, is 24 hr.) (See Section VI.)

2. The cost estimates indicate the operating costs for the electromembrane acid-regeneration process should be competitive with all but the lowest cost processes for disposing of spent pickle liquor. Many plants cannot use the lowest cost existing processes (such as deep-well injection, or direct discharge to sewers after neutralization). Moreover, many of the existing processes (such as neutralization with limestone plus lagooning) produce residues that are not entirely satisfactory for discharge to receiving streams. The only material to be disposed of from the electromembrane process will be hydrous iron oxides (22 to 26% moisture) that are no more harmful to the environment than naturally occurring iron ores. These solids can be disposed of by low-cost earth-fill methods. (See Section 7.)

Other conclusions are:

3. Service lifetimes of MC 3142 and MA 3148 membranes* could be as long as 2 yr (based on the data of Kramer[1] and Forgacs[2]). (pp. 17 through 20.)

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*Ionac Chemical Company, Birmingham, New Jersey.

4. The method of removing iron from spent pickle liquor that involves the formation of insoluble iron hydroxides is more practical for use than the method that involves plating of iron onto cathodes. (pp. 21 through 24.)

5. The resistance of unit cells decreases with increasing temperature, and it will be important to operate the process at as high a temperature as possible to minimize energy costs. (pp. 28 through 30.)

6. The probable maximum temperature of operation is 70°C, since there is evidence that the glass-transition temperatures of MC 3142 and MA 3148 membranes are only slightly higher than 70°C and ion-exchange membranes lose their desirable properties when the glass-transition temperature is exceeded. (pp. 17 through 20.)

7. It should be possible to achieve coulomb efficiencies of at least 50% when the process is operated on a large scale. Coulomb efficiencies from 50% to 70% were achieved in the laboratory. (p. 52.)

8. The specific permselectivity of H^+ and Fe^{+2} ions through MC 3142 cation-exchange membranes is 1.7 ± 0.4. The specific permselectivity is a convenient parameter for use in designing continuous processes. (pp. 57 through 60.)

9. For full-scale acid-regeneration processes, it should be possible to achieve average current densities of 48 to 55 mA/cm^2 with cell voltages of 5 V and temperatures of 65° to 70°C. (pp. 30 and 52.)

10. The insoluble iron hydroxides formed in the electromembrane process are easily separated from the Na_2SO_4 solution. They settled to 50% of the total volume in 30 min and to 25% of the volume in 60 min. (p. 44.)

II. RECOMMENDATIONS

On the basis of the foregoing conclusions it is recommended that research on the electromembrane process for regenerating usable pickling acid from spent pickle liquor be continued to study the long-term behavior of the cell and membranes on a pilot-plant scale. For the most effective studies, the pilot plant should be located at one of the industrial sponsors plants and should operate on the actual pickle liquor produced at the plant. Simultaneously, studies in the bench-scale cell would be performed to study the effects on cell performance of particular components in actual pickle liquors from other sources including the liquors from other industrial sponsors.

III. INTRODUCTION

This report covers the research performed to study an electromembrane process for treating spent sulfuric acid pickle liquor to produce usable acid. The objectives of the research were to determine the technical feasibility of an electromembrane process for regenerating usable sulfuric acid from spent pickle liquor, to develop engineering data for the design of larger units, and to prepare cost estimates based on the experimental findings to indicate the economic feasibility of the process.

The rationale of the research program was based on the following considerations:

In the pickling of steel products with H_2SO_4, iron oxides are dissolved from the surfaces of the products and H_2SO_4 is converted to $FeSO_4$. The pickling solution is normally used until its content of $FeSO_4$ is increased and its content of H_2SO_4 is decreased to levels at which efficient dissolution of additional iron oxides from the surfaces of the products is no longer possible. The pickling solution is then considered to be "spent". The pickling rates achievable with 10% to 15% sulfuric acid solutions (the usual range of concentrations in fresh pickling acid) become slower as iron is dissolved and become unacceptably slow when the ferrous sulfate concentrations reach the range of 15% to 20% with corresponding remaining acid concentrations of 2 to 5%.

If usable pickling acid is to be regenerated from spent pickling liquor, iron ions must be removed from the liquor and replaced by hydrogen ions. The iron ions can be replaced by hydrogen ions by an electromembrane process. Removal of the dissolved iron can then be facilitated by conversion to a solid form that can be readily separated from solutions. Two promising ways for accomplishing this in an electromembrane cell were studied. One way was to plate the iron on the cathode in a loosely adherent form; the other was to convert the dissolved iron to iron hydroxides that could be separated from solution by filtration or settling. Therefore, an electromembrane process seemed to offer considerable promise for treating spent pickle liquor to regenerate usable pickling acid and to remove the iron in a solid form that might be used or sold, or, at least, present no serious disposal problems.

IV. SUMMARY

The studies described in this report indicate that either a batch-recycle or a continuous method of acid-regeneration with electromembrane cells is technically feasible and that the operating costs should be competitive with all but the lowest cost existing methods of disposal of spent pickle liquor. The most serious remaining question about the operation of the electromembrane process is the long-term performance of the cell when treating actual pickle liquors that contain organic pickling aids. Only one actual pickle liquor was studied in this program. Further research to study the behavior of large cells during long periods of operation with actual pickle liquors is needed.

The results of studies of ten commercially available membranes indicated MC 3142 cation-exchange and MA 3148 anion-exchange membranes,* both products of the Ionac Chemical Company, have the best physical and electrochemical properties of the membranes studied for the proposed use. These studies suggest that these membranes might have useful service lifetimes of 2 years, or more, under the expected conditions of service and that 70°C would probably be the maximum permissible operating temperature because the transport properties of both the MC 3142 and MA 3148 are seriously degraded above that temperature.

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*We have used the terms cation- and anion-exchange membranes throughout this report in preference to other nomenclature found in the literature (e.g. cationic membranes, cation-selective membranes), since a standard reference book, "Ion Exchange" by F. Helferrich (McGraw-Hill), uses cation-exchange in preference to other terms.

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Studies of plating iron from iron sulfate solutions were made under a variety of operating conditions (current densities from 25 to 100 mA/cm^2, temperatures from 50°C to 80°C, and with the pH of the solution at 2.0 and 3.6). The results of these studies indicate that it will be difficult to deposit the iron on cathode materials (seven different materials were tried) in a loosely adherent form so that it can be easily and cheaply removed. The results of other studies indicate that the iron from spent pickle liquor can be converted to readily separable insoluble iron hydroxides in an electromembrane cell and that H^+ ions can be generated at the anode of the same cell simultaneously to replace the iron ions that were removed from the pickle liquor. These results indicate that the preferred method of removing iron from spent pickle liquor is the method that involves the formation of iron hydroxides.

Data from further studies of the electromembrane process in which hydrous iron oxides are formed and removed by filtration or settling show that coulomb efficiencies for acid production in the anolyte compartment of three-compartment unit cells can reasonably be expected to be 50%, or higher (coulomb efficiencies from 50% to 70% were obtained in the experiments).

Either a batch-recycle method, which is described on pages to , or a continuous method, which is described on pages to , appear to be technically feasible. For either method, three-compartment cells formed by an anode, an anion-exchange membrane, a cation-exchange membrane, and a cathode would be used.

For the batch-recycle method, the spent pickle liquor would be circulated from a storage tank through the center compartment (bounded by the two membranes) from which iron ions would transfer to the catholyte compartment and sulfate ions to the anolyte compartment. A solution of Na_2SO_4 (about 7% by weight) would be circulated through the catholyte compartment, where Na^+ ions would be discharged at the cathode to form sodium metal which would react with water to form NaOH. The OH^- ions would react with the iron ions transferred through the cation-exchange membrane to form insoluble iron hydroxides, which would be filtered from the Na_2SO_4 solution before recirculation. A solution from which the iron had been removed during a previous time cycle would be circulated

through the anolyte compartment where the sulfate ions entering through the anion-exchange membrane would combine with H^+ ions formed at the anode to regenerate H_2SO_4. After the iron had been removed from the pickling solution during the circulation through the center compartments of the cells and the H_2SO_4 had been regenerated during the circulation through the anolyte compartments, the pickling solution would be ready for reuse as pickling acid.

The continuous process would operate in a similar manner in that pickle liquor from the pickling operation would be circulated through the center compartment and iron ions would be transferred through the cation-exchange membrane into the catholyte solution where insoluble iron hydroxides would be formed. However, in the continuous process the pickle liquor would flow directly to the anolyte compartment as soon as it left the center compartment. In the anolyte compartment, H_2SO_4 would be formed in an amount equal to the iron ions removed through the cation-exchange membrane. The pickling acid would then be returned to the pickling operation.

The continuous method is slightly simpler than the batch-recycle method, but both methods might find use depending on whether the pickling operation is a continuous or batch process.

Of the cell voltages studied (4, 4.5, 5, and 6 volts), voltages of 4.5 or 5 volts appeared to offer the best combination of reasonably rapid regeneration rates and reasonably high coulomb efficiencies, and estimates of processing costs were prepared with those two assumed cell voltages. In the cell used for these studies the spacings between membranes (or between a membrane and an electrode) were 0.125-in. and the temperatures were 55° and 60°C.

The cost estimates indicated that the probable operating costs for the acid regeneration process would be equivalent to about $0.043 to $0.047/gal. of spent pickle liquor for intermediate and large pickling operations (2500 and 6700 gpd). These costs should be competitive with all but the cheapest existing processes for disposing of spent pickle liquor, since the total costs of purchasing acid and disposing of spent liquor by existing processes are from $0.015 to $0.060/gal. This range is based on costs of $0.01 to $0.02/gal. for purchasing acid plus $0.005 to $0.040/gal. for disposal as shown below.

Method	Cost, $/gal.
Deep-well injection	0.005 to 0.01
Neutralization and lagooning	0.01 to 0.02
Neutralization and land-fill	0.02 to 0.03
Hauling	0.02 to 0.04

The cheaper processes for disposal (e.g. deep-well disposal or neutralization and lagooning) cannot be used at all locations, nor under all circumstances. With the electromembrane process, the only material to be disposed of is solid iron hydroxide, which is no more damaging to the environment than iron ore. Moreover, it may be possible to sell the solid iron hydroxide for credits to offset the cost of disposal.

V. EXPERIMENTAL

Preliminary studies were made to determine the important properties of available ion-exchange membranes, to select the best membranes for use in subsequent experiments, and to determine whether plating of iron onto cathodes or a method that involved the formation of insoluble iron hydroxides was the better method for converting the iron removed from the spent pickle liquor by electrolysis to a solid form that could be separated easily. Experiments were then made in bench-scale apparatus to determine the relationships between the main controllable operating variables (voltage and temperature) of the selected process and the main performance factors (current density and coulomb efficiency), to check the stabilities of the materials used in the electromembrane cell, and, finally, to determine whether there are any materials in actual pickle liquor that would cause the electromembrane cell to perform differently than with the solutions of $FeSO_4$-H_2SO_4 with which the previous experiments were performed.

In addition to the above experiments that were concerned with the performance of the cell itself, experiments were performed to determine the settling rates of the iron hydroxides produced in the bench-scale cell to provide data with which the costs of solids separations equipment for use in the full-scale process could be estimated.

A. Preliminary Studies

1. Membrane properties and selection of membranes

The more important properties of the ion-exchange membranes that were available were determined so that the best membranes for use in subsequent studies could be selected. The most important membrane properties for the proposed use in an electromembrane process for regeneration of sulfuric acid were (a) the transport numbers of H^+ and Fe^{+2} ions through cation-exchange membranes, (b) the transport numbers of H^+ and SO_4^{-2} ions through anion-exchange membranes, (c) the resistances of the membranes when equilibrated in solutions containing $FeSO_4$ and H_2SO_4, and (d) the physical and electrochemical stabilities of the membranes when in contact with solutions of $FeSO_4$ and H_2SO_4 at the temperatures anticipated for use (50°C to 70°C).

Experimental determinations were made of the transport numbers and resistances of the membranes under selected conditions, but for information about the stabilities of the membranes under conditions of anticipated use, we depended on the previously developed data of Kramer.[1]

a. Determination of transport numbers of membranes

The cell used to determine transport numbers consisted of two identical, half-cells made of Micarta plastic laminate from Westinghouse Electric Corporation. Each half-cell contained a 3x3-in. graphite electrode. When the membrane to be tested was clamped between the two half-cells, the membrane separated two 3x3x0.125-in. solution compartments formed by cavities adjacent to the electrodes. Each solution compartment had a solution entrance manifold at the bottom and an exit manifold at the top. A schematic diagram of the cell and its auxiliary equipment is shown in Figure 1.

In a typical determination of the transference numbers of H^+ and Fe^{+2} ions through cation-exchange membranes, or of H^+ and SO_4^{-2} ions through anion-exchange membranes, the solution loop through the anode side of the cell was charged with 3 liters of anolyte solution, which contained about 10% of $FeSO_4$ and 5% of H_2SO_4. The solution loop through the cathode side of the cell was charged with 3 liters of catholyte solution, which contained about 5% of $FeSO_4$ and 4% of H_2SO_4. The solutions were circulated through the respective compartments and voltage was applied to the electrodes for a timed period of about 2 hours, during which time the current was maintained at 100 mA/cm^2 and the temperature was maintained at 60°C. Samples of the anolyte and catholyte solutions were taken at the start and end of the timed period and analyzed for Fe^{+2}, Fe^{+3}, and H^+. From the change in the compositions of the two solutions and from the number of coulombs passed through the cell, the transference numbers of H^+ and Fe^{+2} ions (as eq/F) in the membrane being tested or of H^+ and SO_4^{-2} ions, were calculated.

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1. R. M. Kramer, "Electrodialytic Concentration of Sulfuric Acid", Ph.D. Dissertation, Chemical Engineering Department, Polytechnic Institute of Brooklyn (1963).

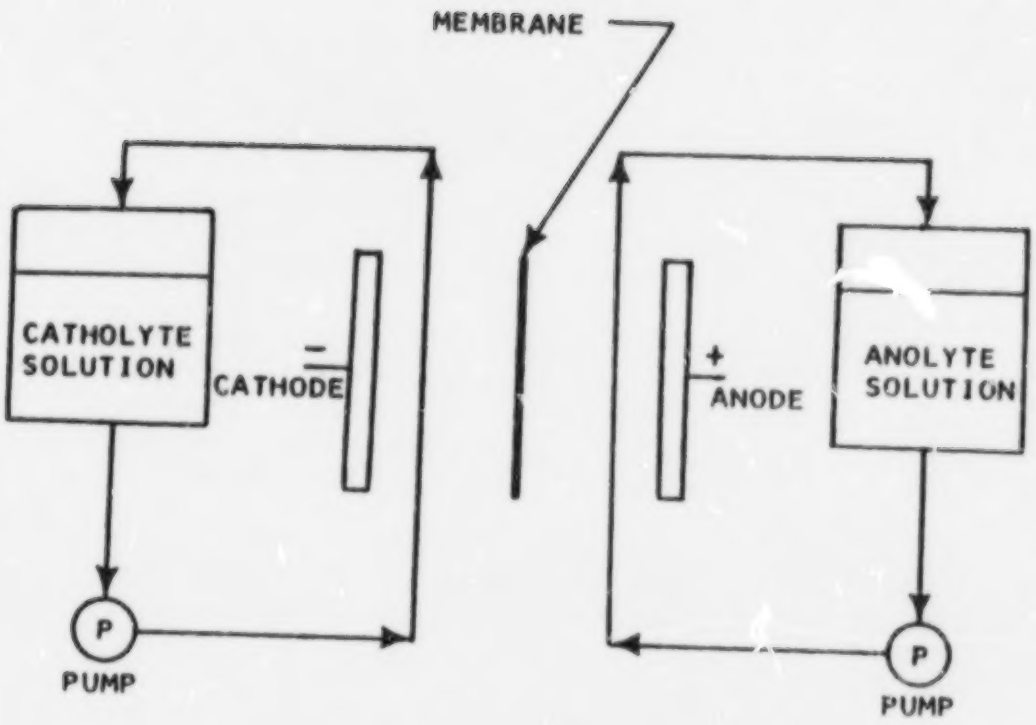

Figure 1. Diagram of Cell and Auxiliary Equipment Used to Determine Transference Numbers of H^{+} and Fe^{++} Ions

A few difficulties were encountered during the first several experiments. In the anolyte solution, Fe^{+2} ions were oxidized to Fe^{+3} ions in a non-reproducible manner, probably because of the oxygen gas evolved at the anode of the cell. This oxidation reaction produced H^+ ions also, so that the values of transference numbers calculated from changes in the composition of the anolyte solution were unreliable and not reproducible. However, the formation of H^+ and Fe^{+3} ions in the anolyte solution did not affect the compositions of the catholyte solutions and good material balances of the Fe^{+2}, H^+, and SO_4^{-2} ions were obtained from the chemical analyses of the initial and final samples of the catholyte solutions.

The following analytical methods were found to be reliable for use in our studies. Difficulties were encountered with the first methods used for analysis of the solutions for H_2SO_4 because of the presence of the hydrolyzable Fe^{+2} and Fe^{+3} ions, but the methods described below proved to be satisfactory.

- For Fe^{+2} ions - The potassium permanganate method described by Joseph Rosin, "Reagent Chemicals and Standards", Van Nostrand, N.Y., 1967, p. 206.

- For Fe^{+3} ions - A method involving the reduction of all Fe^{+3} to Fe^{+2} followed by a potassium permanganate titration that is described by Koltoff and Belcher, "Volumetric Analysis", Vol. 3, Interscience, N.Y., 1957, p. 83.

- For H^+ ions - Several methods for the determination of H^+ ions in the presence of the hydrolyzable Fe^{+2} and Fe^{+3} ions were studied. The method of Moskowitz, Dasher, and Jamison, Anal. Chem. 32, 1362 (1960) was found to give acceptable accuracy and to be quick and simple enough for use as a routine method for obtaining values for calculation of transference numbers. In this method, the hydrolyzable ions are complexed by the addition of a measured amount of NH_4F so they do not interfere with the subsequent titration with standardized NaOH solution.

The basis for the determination of transference numbers is illustrated below with cation-exchange membranes. The transference numbers for anion-exchange membranes were calculated by similar methods. During electrolysis in the cell shown in Figure 1, the following changes in composition would be expected in the catholyte solution. (The difficulties with oxidation in the anolyte solution were mentioned previously.)

- 1 eq/F of H^+ ions would be converted to hydrogen gas at the cathode and thus disappear from the catholyte solution. With the pH conditions in the catholyte solution, only H^+ and no Fe^{+2} or Fe^{+3} ions, would be discharged at the cathode.

- t_{H^+} eq/F of H^+ ions, $t_{Fe^{+2}}$ eq/F of Fe^{+2} ions, and $t_{Fe^{+3}}$ eq/F of Fe^{+3} ions would be transferred from the anolyte solution through the cation-exchange membrane into the catholyte solution.

The net change in the H^+ ion content of the catholyte solution would be $(t_{H^+}-1)$ eq/F. The net change in the Fe^{+2} ion content would be $t_{Fe^{+2}}$ eq/F, and the net change in the Fe^{+3} ion content would be $t_{Fe^{+3}}$ eq/F. Thus, knowing the values for the initial volumes and the Fe^{+2}, Fe^{+3}, and H^+ ion contents of the catholyte solution initially and after electrolysis along with the value for the total number of coulombs passed through the cell would permit calculation of t_{H^+}, $t_{Fe^{+2}}$, and $t_{Fe^{+3}}$.

The transference numbers determined by this method for the ten membranes considered for use in this program are given in Table I.

b. Determination of membrane resistances

The cell used for the determinations of areal resistances of the ion-exchange membranes consisted of two identical half-cells. Each half-cell was a 3x3-in. piece of 1-in. Micarta plastic laminate (from Westinghouse Electric Corporation) provided with a 0.500-in. diameter cavity centered on one of the 3x3-in. surfaces. The cavity was 3/16-in. deep. The bottom of the cavity was covered with a disk (0.500-in. diameter) of platinum to serve as an electrode. A platinum wire, to serve as an electrical connection, was spot-welded to the disk and led through a small hole in the Micarta laminate. This small hole was subsequently filled with Silastic

Table I. Transport Properties of Ion-Exchange Membranes Considered for Use in the Process

Membrane designation	Supplier	Transference number[a] For H^+	For Fe^{+2}	For SO_4^{-2}	Resistances,[b] ohm-cm² In 1.5% H_2SO_4 and 10% $FeSO_4$	In 10% H_2SO_4 and 5% $FeSO_4$
Cation-exchange						
MC 3142	Ionac Chemical Co.	0.5	0.5	0.0	7 to 9	0.5 to 1.0
MC 3470	Ionac Chemical Co.	0.8	0.2	0.0	35 to 49[c]	d
CSV	Tokuyama Soda Co., Ltd.	0.8	0.2	0.0	17 to 40[c]	1.7
CL-2.5T	Tokuyama Soda Co., Ltd.	0.5	0.5	0.0	4 to 8	d
CMV-2	Asahi Glass Co., Ltd.	0.8	0.2	0.0	5	d
AZL183	Ionics, Inc.	0.8	0.2	0.0	7 to 8	0.6
Anion-exchange						
MA 3148	Ionac Chemical Co.	0.4	0.0	0.6	11 to 18	1 to 2
AV-4T	Tokuyama Soda Co., Ltd.	0.4	0.0	0.6	4	d
AST-2	Asahi Glass Co., Ltd.	0.6	0.0	0.4	12	d
BZL183	Ionics, Inc.	0.4	0.0	0.6	6 to 12	1.2

a. Measured at 60±1°C with an anolyte solution containing about 10% of $FeSO_4$ and 5% of H_2SO_4, and a catholyte solution containing about 5% of $FeSO_4$ and 4% of H_2SO_4.

b. Measured at 60±1°C. Varied with current density.

c. Resistance increased with time.

d. Not measured.

RTV cement to seal it. Each half-cell was also provided with one tube at the bottom and one at the top to introduce and withdraw solutions.

In operation, two half-cells were clamped together with the membrane to be tested between them so that each cylindrical cavity had an electrode at one end and a surface of the membrane at the other. The inlet tubes to the half-cells were connected with tubing to a pump, and thence to a reservoir that contained a solution containing 10% of $FeSO_4$ and 1.5% of H_2SO_4. The outlet tubes from the half-cells were returned to the reservoir so that the solution would circulate through each half of the cell when the pump was on. The entire system was maintained at 60±1°C.

For measurements, the solution was circulated through the cell, a d-c voltage to the electrodes was increased stepwise, and the electrode voltage and the current were recorded for each value of electrode voltage. When a sufficiently high current density was reached (ca 300 to 400 ma/cm^2), the voltage was decreased stepwise and the electrode voltage and current were again recorded at each value of electrode voltage.

The cell was then disassembled and the test membrane was removed. The two half-cells were reassembled, but this time without a membrane, and the electrode voltage required for each current density recorded without the membrane in the cell was determined. The areal resistance (in ohm-cm^2) of the test membrane was calculated from the difference between the cell voltages with and without the membrane, the current density, and the area of membrane exposed to the current (1.226 cm^2).

The entire procedure was then repeated in an identical manner except that the solution contained about 5% of $FeSO_4$ and 10% of H_2SO_4 (instead of 10% of $FeSO_4$ and 1.5% of H_2SO_4).

The values for the resistances of the membranes considered for use in this program are given in Table I.

c. Stability of membranes in H_2SO_4

Two of the membranes for which data are given in Table I (the CMV-2 and the AST-2 membranes made by the Asahi Glass Co., Ltd.) showed some evidence of physical degradation during the relatively brief exposures to the $FeSO_4$-H_2SO_4

solutions (at 60°C) that were used in the above procedures. The estimated cumulative time of exposure was 6 hours. There was no evidence of degradation of the other membranes.

Kramer has presented data on the physical and electrochemical stabilities of a number of ion-exchange membranes after exposure to sulfuric acid solutions similar to those proposed for use in the electromembrane regeneration process.[1] Kramer measured the transport numbers and resistances characteristic of various ion-exchange membranes before and after various periods of exposure of the membranes to H_2SO_4 solutions at 50°C and at 80°C. The differences in the measured properties were considered to indicate the degree of degradation of the electrochemical (i.e. transport) properties of the membranes. He used a concentration potential method for determining transport numbers in which the membranes separated 1 N and 0.5 N solutions of KCl, and resistances were measured with the membranes equilibrated in 0.5 N KCl. He expected that measurements in KCl solutions would indicate changes in the characteristics of the membranes better than measurements in H_2SO_4 solutions.

Along with a number of other membranes, Kramer evaluated the MC 3142 and MA 3148 membranes.* His data for these membranes are given in Table II with his data for the membranes he selected as the most stable of those that he evaluated, C-60 and A-60. The C-60 and A-60 membranes, which were manufactured by American Machine and Foundry Company, are no longer available.

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*From the Ionac Chemical Company.

Table II. Stability of Ion-Exchange Membranes in 1 N H_2SO_4 Solutions at Elevated Temperatures

Membrane designation	Transport properties of membranes: After storage at 50°C for 0 months		After storage at 50°C for 4 months		After storage at 50°C for 9 months		After storage at 80°C for 0 months		After storage at 80°C for 4 months		After storage at 80°C for 8 months	
	t^a	R^b	t^a	R^b	t^a	R^b	t^a	R^b	t^a	R^b	t^a	R^b
MC 3142[c]	0.94	8	0.85	6	0.86	6	0.98	8	0.73	6	0.76	5
MA 3148[c]	0.90	9	0.87	7	0.88	9	0.90	16	0.80	12	0.79	11
C-60[d]	0.92	4	0.86	2	0.86	3	0.92	2	0.83	2	0.87	2
A-60[d]	0.94	8	0.93	8	0.93	6	0.93	7	0.91	4	0.91	4

a. Transport number of the counterion measured by a concentration-potential method when the membrane separated 1.0 N and 0.5 N KCl.

b. Resistance in ohm-cm^2 when the membrane was equilibrated in 0.5 N KCl.

c. From Ionac Chemical Company, Birmingham, New Jersey.

d. From American Machine and Foundry Company, Stamford, Connecticut.

The data in Table II indicate that, at 50°C the MC 3142 cation-exchange membrane was essentially as stable as the C-60 cation-exchange membrane. However, the decrease in transport number of the MC 3142 membrane during 8 months of storage in H_2SO_4 solution at 80°C was significantly larger than the decrease in the transport number of the C-60 membrane.

Similarly, the MA 3148 membrane was almost as stable as the A-60 membrane when stored for 9 months in 1 N H_2SO_4 solution at 50°C, but was significantly less stable than the A-60 membrane when stored at 80°C.

Kramer pointed out that the glass-transition temperatures of some of the membranes he tested were less than 80°C and he attributed the decreases in transport numbers of such membranes when stored at 80°C to changes in the structure of the polymers that occurred when the glass-transition temperature was exceeded.

In extended tests, Kramer also showed that the transport properties of the C-60 and A-60 membranes declined only slightly during 2 years storage in 1 N H_2SO_4 solution at 80°C, which suggests those membranes might have usable lifetimes of 2 years.

Judging from these indications of the stability of the MC 3142 and MA 3148 membranes when stored at 50°C, these membranes should have acceptably long lifetimes (perhaps 2 years) if used in the proposed electromembrane process at 50°C.

Forgacs[2] used MC 3142 and MA 3148 membranes to desalt NaCl solutions by electrodialysis at temperatures of 70°C and 90°C. He found that the MC 3142 and MA 3148 membranes retained their transport properties in long-term experiments when the operating temperature was 70°C, but the transport properties deteriorated in experiments at 90°C.

The results of both Kramer and Forgacs suggest that the glass-transition temperature of the MC 3142 and MA 3148 membranes is slightly above 70°C and that these membranes should have acceptable lifetimes when used in H_2SO_4 solutions at 70°C or less. As stated before, there is a suggestion in Kramer's data that the usable lifetimes might be 2 years, or longer.

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2. C. Forgacs, Desalination 3, 129 (1967).

Considering all of these data on the transport properties and the stabilities, we selected the Ionac MC 3142 and MA 3148 membranes as the main ones for our further studies.

2. Studies of methods of conversion of iron to a solid form for removal

At the outset of this program two methods for converting the iron removed from the spent pickle liquor to a readily handled solid form were considered: plating the iron out onto cathodes and precipitation as iron hydroxides. Plating the iron out appeared to be the simpler. However, to be successful it would be necessary to form loosely adhering deposits that could be removed easily from the cathode and also necessary to prevent the growth of dendrites on the electrodes that could puncture the ion-exchange membranes. In the method involving conversion to insoluble hydroxides, the major problems appeared to be (a) the development of an easy method of partially oxidizing the ferrous iron to ferric iron so that easily filterable iron hydroxides (presumed to be ferroso-ferric hydroxides) could be formed, since either ferrous or ferric hydroxides by themselves form as gelatinous precipitates that are hard to filter, and (b) the development of an electromembrane cell in which insoluble hydroxides would not form within the membranes and increase the electrical resistance of the cell.

We studied both of these methods.

a. Plating

(1) Comparison of various cathode materials

The plating experiments were performed by immersing a small rectangular piece (typically 12 x 10 cm) of the cathode material to be studied in a solution of $FeSO_4$ (typically 15% of $FeSO_4$) along with a graphite anode. The cathode and anode were held 3 cm apart by a Micarta spacer. Voltage was applied to the cells and adjusted to give the desired value of current density in the range of 50 to 100 mA/cm^2, while the $FeSO_4$ solution was maintained at the desired temperature (50°C or 60°C). Experiments were made with $FeSO_4$ solutions with a pH of 3.6 and a pH of 2.0.

Electrodeposition on the cathode was carried out for 2 hours and then the cathode was removed from the bath, rinsed, and the deposit of iron was examined to note the approximate length, number, and location of any dendrites formed, and the tenacity with which the deposited iron was attached to the cathode material. It was planned that more quantitative means of determining the adherence of coatings would be used for the cathode materials that showed some promise in the initial visual screening tests, but none of the materials studied showed enough promise to warrant further study.

The cathode materials studied were: low-carbon steel, Armco iron with extremely low carbon content, 316 stainless steel, 430 stainless steel, aluminum, chrome-plated steel with a matte finish and with a mirror finish, and titanium.

In these initial studies, titanium was the only cathode material of those studied to which the deposited iron adhered only loosely. Tightly adherent deposits with dendrites formed on all of the other cathode materials.

(2) Studies with titanium cathodes

In further studies with titanium cathodes, the temperature of the $FeSO_4$ solution was varied from 50°C to 80°C, and pH of the solution was either 2.0 or 3.6, and the current density was varied from 25 to 100 ma/cm^2 in attempts to find conditions that would result in deposits of iron that were completely free of dendrites and that could be easily and completely removed from the titanium (e.g. by rapping the cathodes or by simple scraping procedures). No operating conditions were found that resulted in deposits that could be completely removed by simple, low-cost procedures. Moreover, dendrites or other protuberances were formed in all of the experiments. These experiments were stopped when the results of experiments (described later) showed that iron would be precipitated from solutions simulating spent pickle liquor in the form of readily filterable iron hydroxides.

b. Precipitation as hydroxides

(1) Experiments in two-compartment cell

Seven experiments were performed in a two-compartment cell to explore various conditions for the removal of iron from solutions containing sulfates of iron by electrolysis and precipitation of insoluble iron hydroxides. The information obtained in these experiments was mainly qualitative in nature so the experiments will be only briefly discussed.

The main components of the cell used in these experiments were an anode, a cathode, and an Ionac MC 3142 cation-exchange membrane. The cation-exchange membrane was clamped between two identical half-cells to form an anolyte solution compartment and a catholyte-solution compartment. Each compartment was provided with means of introducing and withdrawing solutions from the compartment and contained a graphite electrode.

A ferrous sulfate solution (ferric sulfate in one experiment) was circulated through the anolyte-solution compartment; the concentration of the solution was varied from experiment to experiment over the range of 1% to 10% of ferrous sulfate. A solution of Na_2SO_4 was circulated through the catholyte solution compartment in some experiments; a solution of $(NH_4)_2SO_4$ was circulated through this compartment in other experiments. The catholyte solutions were 1.0 N, except in Experiment 5723-59-1, in which a 0.1 N solution was used. The current density was 100 mA/cm^2 and the temperature was 60°C in all of the experiments. Voltage was applied to the cell for periods varying from 2 hours to almost 7 hours in the several experiments. Samples of the anolyte were taken at intervals during each experiment and analyzed for total iron and ferrous iron contents. Changes in composition with time were calculated from the analyses. The catholyte solutions were filtered at the end of each experiment and the solid was dried and weighed.

In the anolyte-solution compartment H^+ ions and O_2 gas were formed at the anode and Fe^{+2} ions were oxidized to Fe^{+3} ions, either by gaseous O_2 or by direct electrochemical action. In the catholyte-solution compartment Na^+ ions (except when $(NH_4)_2SO_4$ was used) were discharged at the cathode to form Na which reacted with water to form NaOH. Insoluble iron hydroxides were formed by the reaction of OH^- ions with Fe^{+2} and Fe^{+3} ions transferred into the catholyte-solution compartment through the cation-exchange membrane.

The main things learned in these experiments were:

- Easily filtered iron hydroxides were formed in all experiments except the one in which the anolyte solution contained only ferric sulfate. The use of only ferric sulfate in the anolyte solution resulted in reddish gelatinous precipitates that were difficult to filter.

- The cell voltages needed to produce a given current density (100 mA/cm^2) depended on the concentration of $FeSO_4$ and of H_2SO_4 in the anolyte.

- The use of $(NH_4)_2SO_4$ in the catholyte solutions resulted in slightly lower cell voltages than the use of Na_2SO_4. This behavior is in accord with the higher conductance of $(NH_4)_2SO_4$ solutions.

(2) Studies in three-compartment cell at 60°C

After the preliminary experiments in a two-compartment cell were completed, center frames (one 1/8-in. thick and one 1/16-in. thick) were fabricated to fit between the two end frames and convert the two-compartment cell into a three-compartment cell. Additional studies of methods of reducing the iron content of spent pickle liquor by electrolysis and formation of insoluble iron hydroxides were performed in this three-compartment cell, to determine relationships between cell voltage and current densities, as well as to study the formation of precipitates of iron hydroxide. The cell was assembled with an anion-exchange membrane clamped between the anode end frame and the center frame, and a cation-exchange membrane clamped between the cathode end frame and the center frame. Each compartment had provisions for introducing and withdrawing solution.

We planned initially to use partially oxidized ferrous sulfate solutions from previous studies as feeds to the middle compartment of the three-compartment cell. However, in the initial shakedown experiment with the cell, a fresh $FeSO_4$ solution containing no $Fe_2(SO_4)_3$ was used as feed to the middle compartment, and it was found that a black, easily filterable precipitate of iron hydroxide was formed. Apparently, the $FeSO_4$ in the feed solution

was oxidized sufficiently during the recirculation and electrolytic processes to form a filterable precipitate, instead of the slimy greenish precipitate usually resulting from the formation of ferrous hydroxide. Since a filterable precipitate was obtained, the remaining experiments were made with ferrous sulfate solutions as feeds to the middle compartment.

In all of these experiments a 1 N solution of either Na_2SO_4 or K_2SO_4 was circulated through the catholyte compartment. During electrolysis, the alkali metal ions were discharged at the cathode to form alkali metal, which reacted immediately with water to form an alkali metal hydroxide. The hydroxide ions combined with the iron ions entering the catholyte compartment through the cation-exchange membrane to form insoluble precipitates.

Solutions of $FeSO_4$ ranging between 2% and 7% in concentration were circulated through the center compartment.

A solution of H_2SO_4 was circulated through the anolyte compartment. During electrolysis, sulfate ions entered the anolyte compartment through the anion-exchange membrane and hydrogen ions were formed at the anode as a result of the electrolytic decomposition of water. The result of this transfer and decomposition was an increase in the concentration of the circulating acid with time.

A summary of the experiments that were performed is given in Table III. All of these experiments were conducted at 60°C, for a period of 2 hours, and with a current density of 100 mA/cm^2. Although the MC 3142 and MA 3148 membranes were indicated by previous experiments to be the most probable candidates for eventual use, we included CL2.5-T cation-exchange membranes (which also appeared to be good) in some of these experiments to confirm our choice of the MC 3142 cation-exchange membranes.

Experiments 5723-85, -87, and -89 indicated that the voltage needed to maintain a current density of 100 mA/cm^2 in the experimental cell is decreased when the H_2SO_4 content of the anolyte solution is increased. However, the change in voltage (1.1 volt) between Experiments 5723-87 and 5723-89, with only a small change in H_2SO_4 concentration (11% to 12%), appeared anomalously large.

Table III. Removal of Iron from Solutions of Ferrous Sulfate by Electrolysis and Precipitation of Insoluble Iron Hydroxides
(Current density-100 ma/cm^2; all experiments for 2 hours at 60°C)

Experiment 5723-	Membranes used[a]	Composition of catholyte solution	Initial composition of $FeSO_4$ solution	Approximate composition of anolyte solution	Applied voltage
85	CL2.5-T MA 3148	8.7% K_2SO_4[b]	4% $FeSO_4$	7% H_2SO_4	7.3
87	CL2.5-T MA 3148	8.7% K_2SO_4[b]	4% $FeSO_4$	11% H_2SO_4	7.0
89	CL2.5-T MA 3148	8.7% K_2SO_4[b]	4% $FeSO_4$	12% H_2SO_4	5.9
Changed to different cation-exchange membrane; used same anion-exchange membrane.					
91	MC 3142 MA 3148	8.7% K_2SO_4[b]	4% $FeSO_4$	12% H_2SO_4	8.1
95	MC 3142 MC 3148	8.7% K_2SO_4[b]	2% $FeSO_4$	9% H_2SO_4	8.4
Cell modified to thinner center compartment (1/16-in. instead of 1/8-in.); installed new MC 3142 and MA 3148 membranes.					
105	MC 3142 MA 3148	6.7% Na_2SO_4[c]	7% $FeSO_4$	5% H_2SO_4	7.3
107	MC 3142 MA 3148	6.7% Na_2SO_4[c]	4% $FeSO_4$	12% H_2SO_4	6.3
109	MC 3142 MA 3148	6.7% Na_2SO_4[c]	4.5% $FeSO_4$	7.5% H_2SO_4	6.8

a. MC 3142 and MA 3148 designate cation- and anion-exchange membranes, respectively, obtained from Ionac Chemical Co. CL2.5-T designates a cation-exchange membrane obtained from Tokuyama Soda Co., Ltd.

b. 8.7% K_2SO_4 is 1 N in K_2SO_4.

c. 6.7% Na_2SO_4 is 1 N in Na_2SO_4.

Prior to Experiment 5723-91 the three-compartment cell was re-assembled with an MC 3142 cation-exchange membrane to replace the CL2.5-T membrane used in the three prior experiments. Experiment 5723-91 was then performed under the same conditions as Experiment 5723-89. There was a large increase in cell voltage (5.9 volts with the CL2.5-T membrane, 8.1 volts with the MC 3142 membrane) required to obtain the same current density, which suggested the MC 3142 membrane had higher resistance than the CL2.5-T membrane.

Experiment 5723-95 was intended primarily to determine the effect of a lower concentration of $FeSO_4$ solution on cell voltage. Because of an error in preparing the anolyte solution the concentration of acid in the anolyte solution was not the same as in Experiment 5723-91. Therefore, it is not certain whether the increased voltage in Experiment 5723-95 (8.4 volts compared with 8.1 volts in Experiment 5723-91) was a result of the decreased $FeSO_4$ content, the decreased H_2SO_4 content, or both.

After Experiment 5723-95, the cell was reassembled with a thinner center frame (1/16 in. instead of the previous 1/8-in. frame) and with new pieces of MC 3142 and MA 3148 membranes.

The conditions for Experiments 5723-105, -107, and -109 were chosen to explore a possible batch-recycle method of operation of the eventual process that is described only briefly here but in detail in Section III-C. During a given time period, say 6 hours, in such a batch-recycle process:

- The pickling line would be run with acid that had been regenerated previously.
- The spent pickle liquor from the previous time period would be circulated through the center compartments of cells to reduce the iron and sulfate contents.
- The solution from the previous time period that had been reduced in iron and sulfate contents would be circulated through the anolyte compartments to regenerate pickling acid.

The concentrations of the iron sulfate solutions and the H_2SO_4 solutions in Experiments 5723-105 and -107 were chosen to be representative of the concentrations near the end of the time period for the batch-recycle process (Experiment 5723-107), and near the mid-point of the time period (Experiment 5723-105). The catholyte solution was 1 N Na_2SO_4, since Na_2SO_4 (which is lower in cost than K_2SO_4) would probably be used in commercial practice.

The solution concentrations in Experiment 5723-109 represent the concentrations to be expected at a point in the time period of the batch-recycle process between the mid-point and the end.

The general indications from this series of experiments were that as the H_2SO_4 concentration in the anolyte solution increases, the voltage needed to maintain a constant current density will decrease. Conversely, with a constant voltage applied to the cell the current density will increase as time passes and the H_2SO_4 concentration in the anolyte solution increases.

3. Studies of voltage, current, temperature relationships

In addition to the above experiments at 60°C, experiments were performed at 55°C and at 65°C to determine the relationships between voltage, current, and temperature.

The solutions used in the three compartments of the cell were:

Catholyte - 6.7% Na_2SO_4 (1 N Na_2SO_4)
Center - 4.0% $FeSO_4$
Anolyte - 12.0% H_2SO_4

The membranes used were MC 3142 and MA 3148 membranes from Ionac Chemical Co. The cell spacings (i.e. spacings between membranes or between membranes and electrodes) were:

Catholyte - 0.125 in.
Center - 0.0625 in.
Anolyte - 0.125 in.

The cell voltages at various current densities are shown in Figure 2 for temperatures of 55°C and 65°C. The points for each temperature lie on straight lines that intercept the zero axis at 2.4 and 2.5 volts, respectively.

These values correspond with the values of 2.4 and 2.5 volts reported in the literature[3,4] for the decomposition potentials of such cells. The slopes of the voltage-current curves indicate the effective resistances of the cell were 50 ohm cm^2 at 55°C and 45 ohm cm^2 at 65°C.

4. Discussion

In these experiments to explore the methods of removing iron from iron sulfate solutions by electrolysis and formation of insoluble iron hydroxides, the most important information found was:

- The precipitation method of removing iron seemed better for eventual use than the plating method—primarily because the insoluble hydroxides formed can be removed easily by settling or filtration, whereas the solids formed in the plating method cannot be easily or cheaply removed.
- $FeSO_4$ solutions circulating through the center compartments of three-compartment cells are apparently oxidized sufficiently to allow formation of easily filterable precipitates in the cathode compartment.
- The experimental apparatus used in these experiments needed changes (described later in Section III-C) to improve the accuracy of some of the measurements.

B. Bench-Scale Experiments

The cell and equipment used in the bench-scale studies were designed to study an electromembrane process in

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3. D. J. Lewis and F. L. Tye, J. Appl. Chem. 9, 279 (1959).

4. C. L. Mantell and L. G. Grenni, J. Water Pollution Control Fed. 34, 951 (1962).

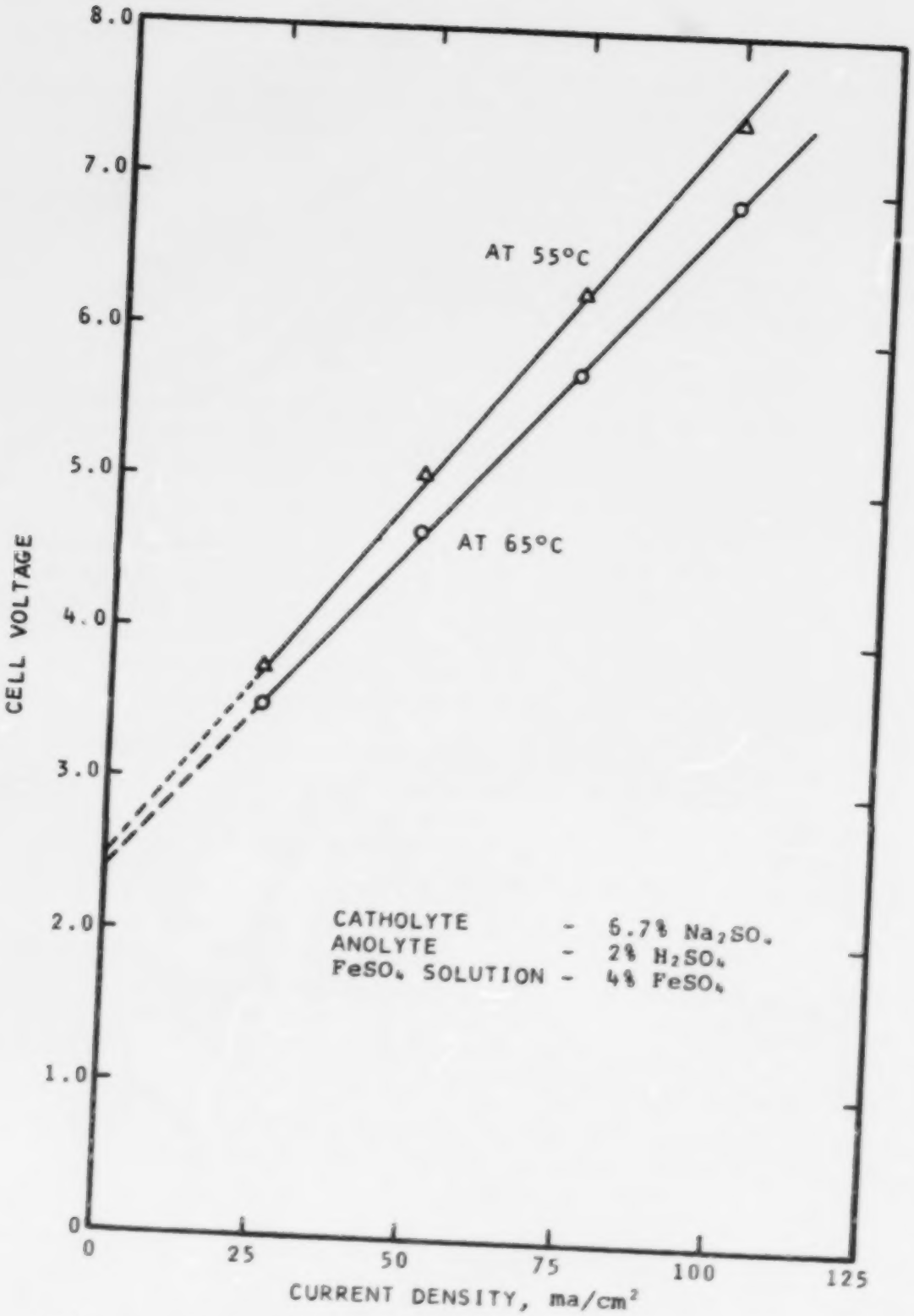


Figure 2. Relationship between Cell Voltage and Current Density at 55°C and 65°C

which iron is removed from spent pickle liquor by electrolysis and precipitated as insoluble iron hydroxides, and acid is regenerated at the anode of cells.

Before describing the equipment and methods used in the experimental program, we will describe a newly conceived electromembrane cell and the way in which it can be used to remove iron from spent pickle liquor and to regenerate acid so that the reader can more easily understand the reasons for the experimental techniques used.

1. Batch-recycle process

a. Prior electromembrane acid-regeneration process

Our considerations of methods of reducing the iron content of spent pickle liquor by a method involving the formation of insoluble iron hydroxides stemmed from our studies of U. S. Patent 3,394,068 (assigned to Ionac Chemical Co.), and a private communication from Mr. Allyn Heit (one of the co-inventors) that described the studies made in support of the patent.

U. S. Patent 3,394,068 points out that the iron content of spent pickle liquor can be reduced by adding OH^- ions to form insoluble iron hydroxides. If it were not for the fact that both ferrous hydroxide and ferric hydroxide precipitate as gelatinous materials that are difficult and costly to filter, the reduction of the iron content by this method would be easy and relatively cheap. However an easily filterable ferroso-ferric hydroxide can be formed if the ferrous ions in the spent liquor are partially oxidized to ferric ions before the formation of hydroxides.

The process described in U. S. Patent 3,394,068 makes use of an electrolytic cell comprised of an anode, a cathode, and two anion-exchange membranes. The two anion-exchange membranes divide the electrolytic cell into an anolyte compartment, a center compartment and a catholyte compartment. A sulfuric acid solution is circulated through the anolyte compartment, the spent pickle liquor (containing iron mainly as $FeSO_4$) is circulated through the center compartment, and a sodium hydroxide solution is circulated through the anolyte compartment. When electrical current flows through the cell: (a) OH^- ions are transferred through one of the

anion-exchange membranes to the center compartment, Na^+ ions are discharged at the cathode, and the sodium reacts with water to re-form NaOH; (b) SO_4^{-2} ions are transferred from the center compartment to the anolyte compartment; and (c) H^+ ions are formed in the anolyte compartment. Thus, OH^- ions are transferred into the pickle liquor, and SO_4^{-2} ions are transferred out of the pickle liquor and insoluble iron hydroxides are formed.

In the process described in U. S. Patent 3,394,068 the coulomb efficiencies achieved for the regeneration of acid were no higher than 30%. Our preliminary experiments indicated higher coulomb efficiencies for regeneration of acid (50 to 70%) could be achieved with a new electromembrane process that differed from that described in U. S Patent 3,394,068.

b. New electromembrane regeneration process

(1) In the new electromembrane process, the three compartments of the electrolytic cells were formed by an anode, a cathode, one anion-exchange membrane, and one cation-exchange membrane (instead of an anode, a cathode, and two anion-exchange membranes). The operation is carried out as a batch-recycle process as described below.

A schematic flow diagram of the batch-recycle regeneration process is shown in Figure 3. Only a single three-compartment cell is shown for convenience in depicting the flows of solutions in the regeneration circuit. In practice, many such three-compartment cells would be assembled into a stack of such cells with appropriate provisions for manifolding the solutions by an arrangement similar to that in a filter press. Stacks such as this, with multiple cells in series, have been used industrially to generate hydrogen and oxygen gases. In the batch-recycle regeneration process, the following operations would be carried out during each of the three steps of a cycle.

- In Step 1, the pickling line would be run with acid that had been regenerated previously. This stream is shown in Figure 3 to be circulating from Tank I to a steam-heated heat exchanger (to avoid the dilution resulting from heating with an open steam line), and then to the

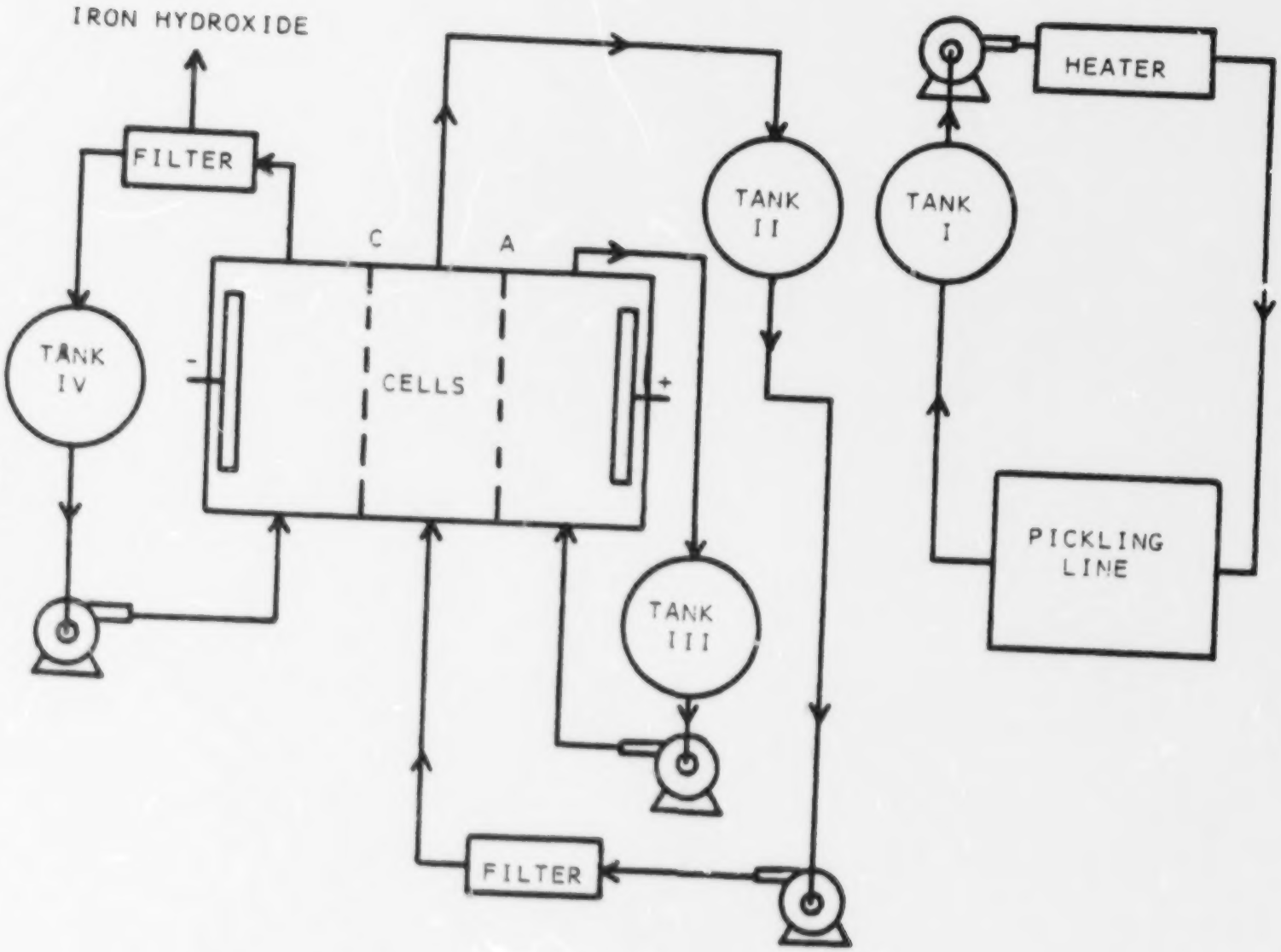


Figure 3. Diagram of Flows in Batch-Recycle Regeneration Process

pickling line and back to Tank I. In this operation, the acid content of the pickling liquor decreases and the iron content increases.

- In Step 2, spent pickle liquor from a previous pickling operation, which is high in iron content and low in acid content, would be circulated from Tank II through a filter to remove particles, such as flakes of mill scale, and then through the center compartments of repeating cells in the regeneration stack and back to Tank II. The iron content of the spent pickle liquor would be reduced in this step.

- In Step 3, the solution in which the iron content was reduced in a previous step would be circulated from Tank III through the anolyte compartments of the cells. In this step, this solution would be enriched in H^+ ions, as a result of the reactions at the electrodes, and in SO_4^{-2} ions, as a result of transfer of SO_4^{-2} ions through the anion-exchange membrane. At the end of the step the solution in Tank III would be ready for reuse for pickling; a small addition of make-up acid might be necessary.

- During Steps 2 and 3, a solution of Na_2SO_4 would be circulated from Tank IV through the catholyte compartments of the cells and then through a filter and back to Tank IV. In the catholyte compartments, Na^+ ions would be discharged to form Na^0, which would immediately combine with water to form NaOH. The OH^- ions would react with Fe^{+2} and Fe^{+3} ions transferred through the cation-exchange membranes to form insoluble iron hydroxides. The iron hydroxides would be filtered and the filtrate, which would be an Na_2SO_4 solution of the original composition, would be returned to Tank IV.

At the end of each step of a cycle, Tanks I, II, and III would be switched to new circulation lines for the next step of a cycle.

(2) Experimental apparatus

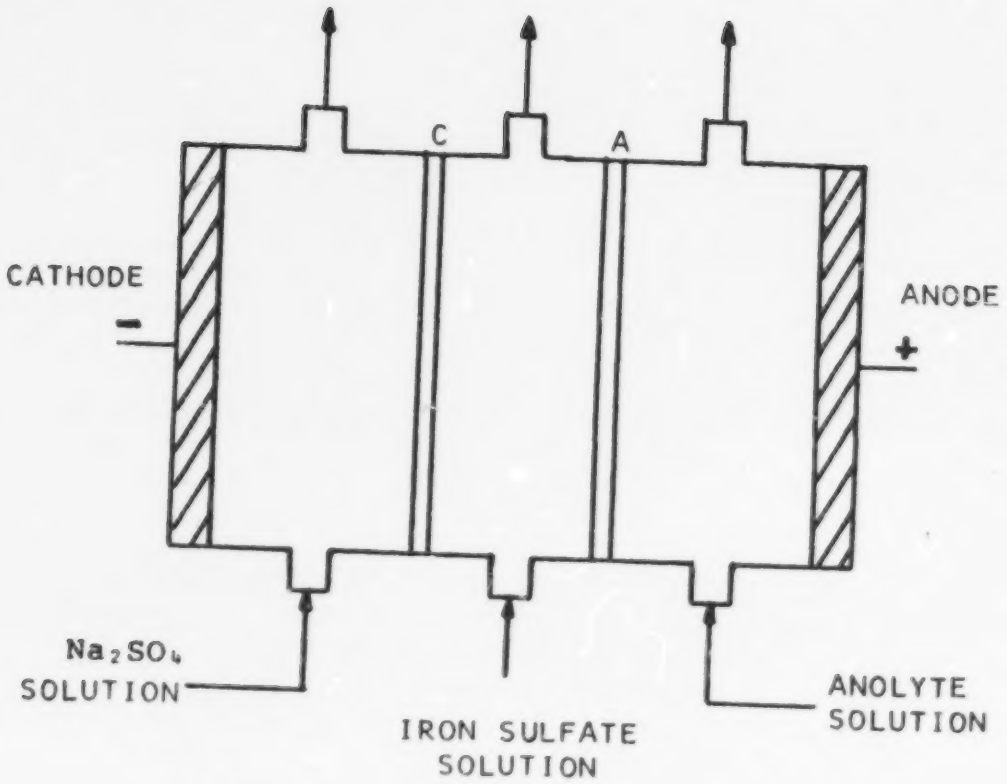
The three-compartment cell used in the experimental studies of the batch-recycle regeneration process is shown schematically in Figure 4. The frame of the cell consisted of two end sections and one center section made of reinforced phenolic resin. The dimensions of the end sections were 1x5x5 in. and each end section had a 0.625x3x3-in. cavity. One cavity was fitted with a 0.5x3x3-in. graphite electrode; the other was fitted with an antimonial lead electrode. The spaces through which the anolyte and catholyte solutions were circulated were each 0.125x3x3 in. These spaces were provided with mesh spacers (Vexar 69-PDS-49 from Du Pont) to support the ion-exchange membranes. Each end-section was also provided with means of introducing and removing solutions and with an electrical connection to the electrode. Graphite was used for the cathode and an antimony-lead alloy was used for the anode.

The center section was 0.125x5x5 in. with a 3x3 in. open space in the center. The center frame was also provided with connections for introducing and removing solutions.

The cell was assembled with an anion-exchange membrane at the anode side of the center section and a cation-exchange membrane at the cathode side to form three solution compartments.

In addition to the cell described above, the auxiliary apparatus included a source of d-c voltage, a reservoir and pump for each of the three circulating solutions, and instruments for indicating—and in some cases, recording—voltages, and current flows. The hydraulic flows are shown in Figure 5.

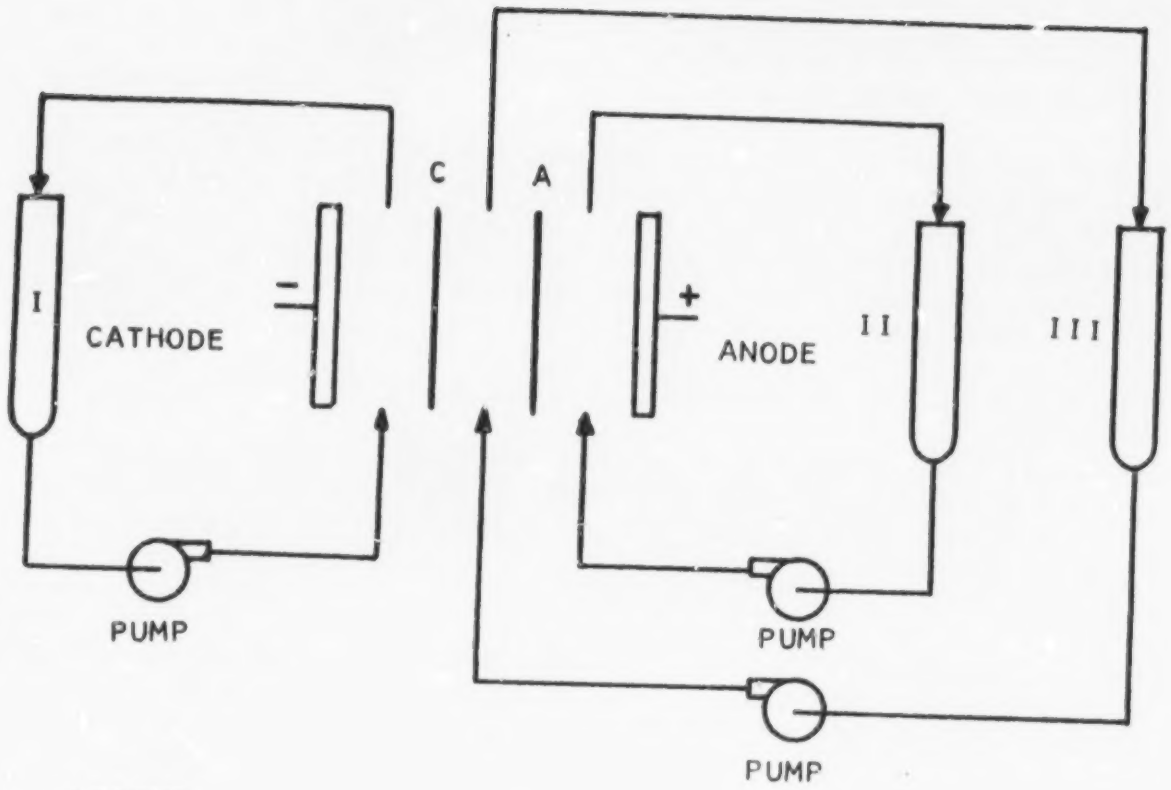
The solution reservoirs were 30 mm in diameter. Solution reservoirs used in preliminary experiments were 3-liter aspirator bottles, but these preliminary experiments showed that small volumes of solution (about 300 ml) were desirable so that large changes in composition could be effected within a reasonable time. Therefore, the reservoirs had to be much smaller in diameter than the 3-liter bottles to improve the accuracy of reading the volumes of the circulating solutions. Initially, electrical heating tapes were wrapped around the reservoirs to provide a means of maintaining the temperatures at 60°C. However, it was found in shake-down



LEGEND:

C - CATION-EXCHANGE MEMBRANE
A - ANION-EXCHANGE MEMBRANE

Figure 4. Diagram of Three-Compartment Cell used in Studies of Batch-Recycle Regeneration Process



LEGEND:

C	-	CATION-EXCHANGE MEMBRANE
A	-	ANION-EXCHANGE MEMBRANE
I	-	RESERVOIR FOR CATHOLYTE SOLUTION
II	-	RESERVOIR FOR ANOLYTE SOLUTION
III	-	RESERVOIR FOR IRON-SULFATE SOLUTION

Figure 5. Hydraulic Flows in Experimental Regeneration Unit

experiments that these tapes were not needed. When the circulating systems were filled initially with solutions at 60°C, the energy input from the pumps and the IR losses in the cells maintained the temperature at 60°±2°C.

The pumps were Eastern Industries, Model D-11 centrifugal pumps. Flow was controlled by a pinch clamp on the rubber tubing at the exit of each pump. The solution flow rates were determined by measuring the amounts of solutions being returned to the reservoirs during a timed interval. With these circulating systems, the estimated uncertainty in the measurements of volume was ±5 ml, or ±2% of the total volume.

The d-c power source was an Eico Model 1060 d-c rectifier. The cell voltage was indicated by a General Electric Type DP-9 voltmeter (1% accuracy) and recorded on a Leeds and Northrup, Speedomax W recorder. The current was indicated by a Weston, Model 931, ammeter (1% accuracy) and recorded on the recorder.

(3) Experiments with Fe_2SO_4-H_2SO_4 solutions

In a typical experiment in the apparatus described above, the composition of the solution circulated through each of the three compartments was chosen to be representative of the composition expected if the process were used in a plant.

The composition of the solution circulated through the center compartment simulated a typical spent pickle liquor—about 10% of $FeSO_4$ and 3% of H_2SO_4 initially. The composition of the solution circulated through the anolyte compartment simulated a typical solution in which the contents of iron sulfate and acid had been reduced in a previous cycle of operation—about 2% of $FeSO_4$ and 0.25% of H_2SO_4. The composition of the Na_2SO_4 solution circulated through the catholyte compartment was 1 N.

Three hundred milliliters of each of the three circulating solutions was preheated to 60°C and placed in the appropriate reservoir of the acid-regeneration unit. The solutions were circulated for 5 to 10 min to remove entrapped air, and then the level of the solution in each reservoir was marked and the temperature of the solution was measured. The normal flow rates of the

circulating solutions were about 30 ml/sec. Voltage was applied to the cell and adjusted to the desired value (either 4, 4.5, 5, or 6 V). Voltages and currents were recorded continuously and also read on the meters at 1-hr intervals. Five-milliliter samples of the iron sulfate solution and the anolyte solution were taken at 1-hr intervals and analyzed later for contents of Fe^{+2}, Fe^{+3}, and H^{+} ions. The levels in the reservoirs were measured each hour.

With these data, the number of equivalents of each ion transferred into or out of each compartment during each time period was calculated and compared with the number of faradays passed through the cell as calculated from the recorded electrical current.

Experiments were performed in the bench-scale equipment to study the batch-recycle acid-regeneration process previously described. The relationships between the controllable variables (applied cell voltage and temperature) and performance factors (coulomb efficiencies and current densities) that are important to the operating costs of the batch-recycle process were studied. These experiments also afforded information about the behavior of materials of construction under operating conditions.

The solutions circulated through the three compartments of the cell were prepared in the laboratory.

Experiments were performed with applied cell voltages of 4, 4.5, 5, and 6 V. The results of these experiments are summarized in Table IV, and are presented graphically in Figure 6. In Figure 6, the current densities and the coulomb efficiencies for the production of H_2SO_4 in the anolyte chamber of the cell are plotted vs cell voltage.

The average current density increased with increasing cell voltage, from about 22 mA/cm^2 with 4 V to about 50 mA/cm^2 with 6 V. The current density curve in Figure 6 was not extended to the 6-V value because of uncertainty as to where it should be drawn. A duplicate experiment was not performed with an applied voltage of 6 V because the lower values of coulomb efficiencies obtained with higher voltages made it seem highly improbable that the process would ever be run on a plant scale with cell voltages as high as 6 V. The data on current densities for cell voltages of 4, 4.5, and 5 V describe a reasonably

Table IV. Coulomb Efficiencies and Average Current Densities with Different Cell Voltages

Experiment 5723-	Cell voltage	Coulomb efficiencies, %		Average current density ma/cm^2
		Center compartment[a]	Anolyte compartment[b]	
119-2	4	71	70	24
120-2	4	71	67	21
120-3	4.5	67	53	33
122-1	4.5	50	61	36
119-1	5 to 6[c]	40	50	47
119-3	5	56	60	45
120-1	5	50	49	39
119-4	6	44	52	50

a. Calculated from the difference between the total equivalents of iron ions at the start and end of the experiment in the solution circulated through the center compartment.

b. Calculated from the difference between the total equivalents of H^+ ions at the start and end of the experiment in the solution circulated through the anolyte compartment.

c. Voltage control was not as good in this experiment as in the others.

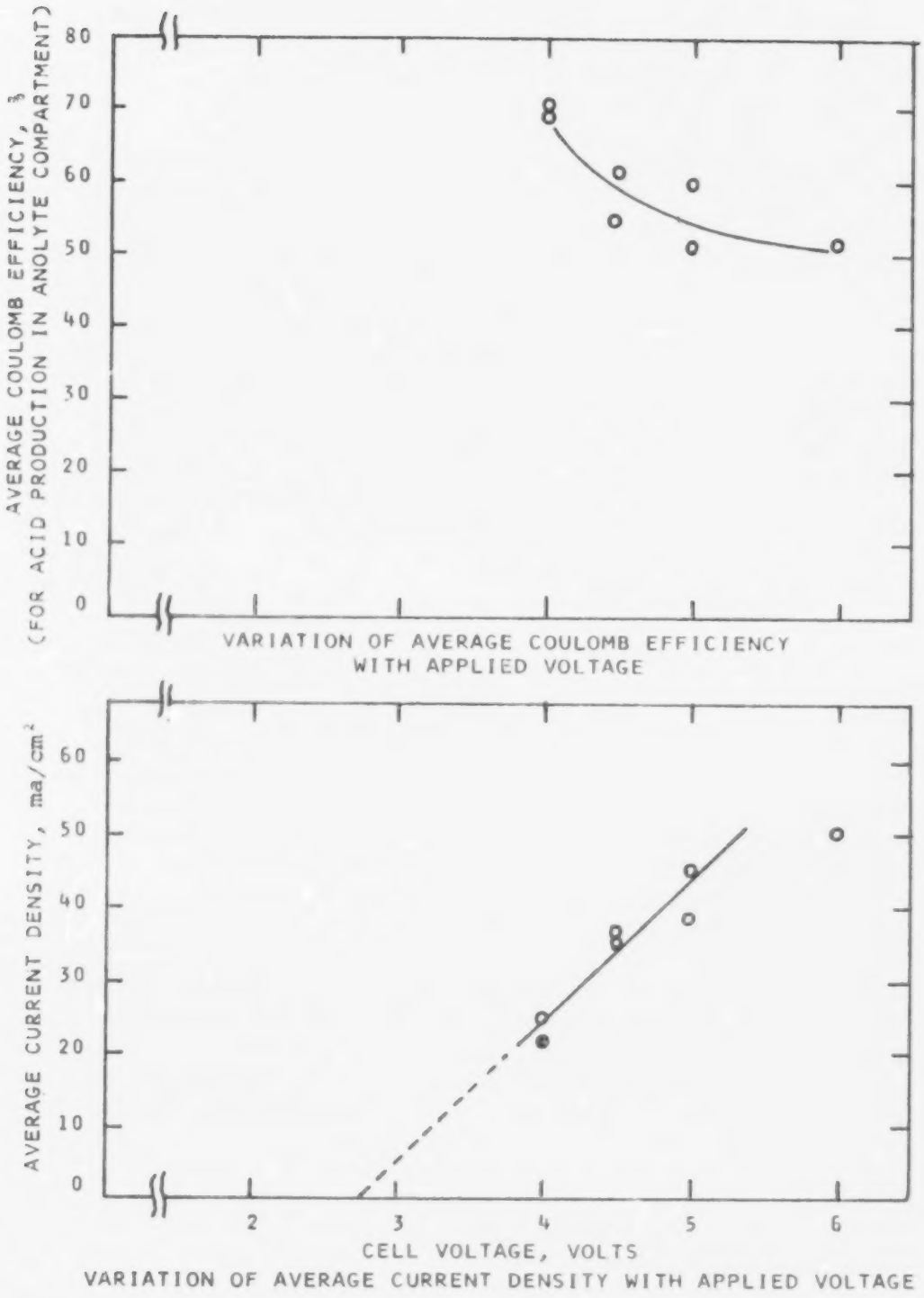


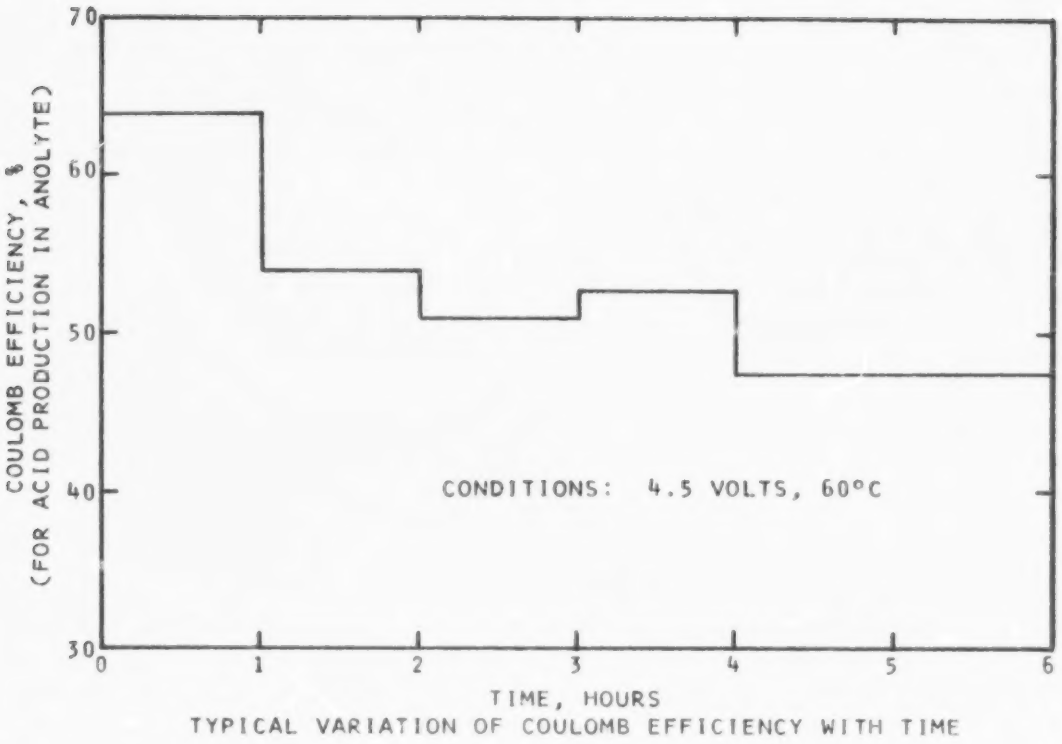
Figure 6. Variations of Average Coulomb Efficiency and Average Current Density with Cell Voltage

good straight line, as expected. However, if the straight line is extrapolated to zero current density, the indicated decomposition potential at the electrodes is about 2.7 V, instead of the 2.4 to 2.5 V found in preliminary experiments. This may indicate the line in the figure should be drawn with a slightly lower slope, but on the basis of the data, it is difficult to justify any lower slope than is shown.

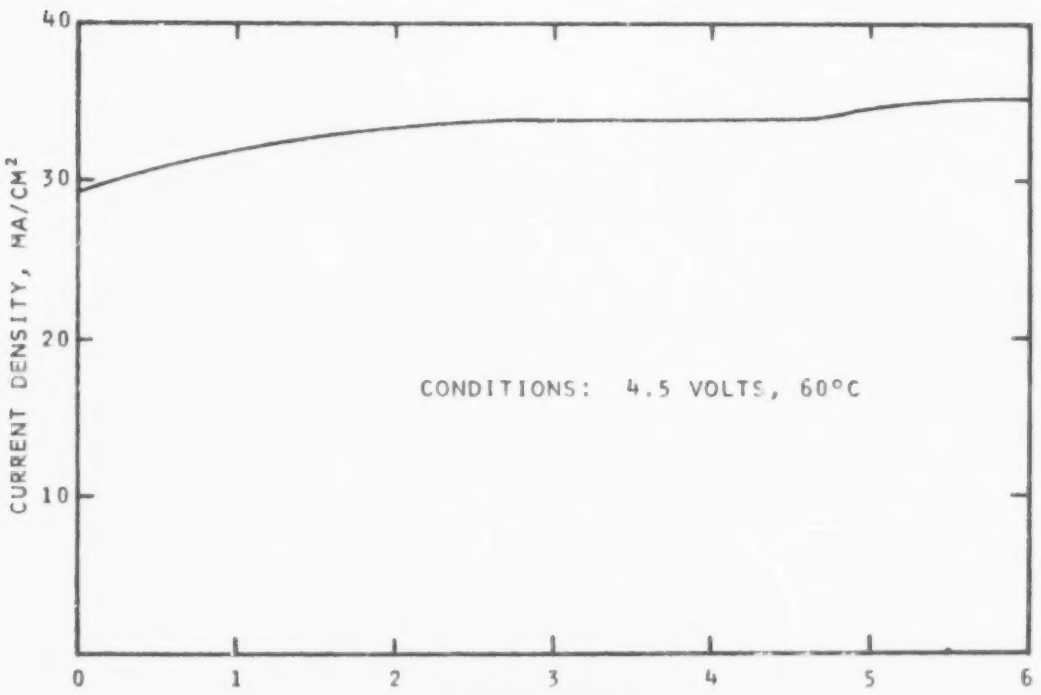
The average coulomb efficiencies (i.e., the averages for the 6-hr periods of the experiments) decreased with increasing cell voltage (and the attendant increasing current density). Almost certainly, one of the reasons for the decrease in coulomb efficiency at the higher voltages is that the acid concentration in the anolyte solution increased to higher values during the 6 hours of each experiment when high current densities (i.e., high voltages) were used. With increasing acid concentrations in the anolyte solution, the anion-exchange membrane separating the anolyte and center solutions becomes more permeable to H^+ ions and more of the H^+ ions formed at the anode are transferred out of the anolyte solution through the anion-exchange membrane.

In addition to the analyses of the experimental data that resulted in the average current densities and coulomb efficiencies reported in Table IV, the current densities and coulomb efficiencies were calculated for each hour of the 6-hr period of operation. Typical variations in current density and coulomb efficiency with time are shown in Figure 7. The variation of current desnity was taken from data printed by the recorder, but the coulomb efficiencies had to be calculated for 1-hr periods and are shown as average efficiencies for each hour.

The current densities usually increased slightly during the course of the 6-hr runs, as indicated in Figure 7. This increase in current density is believed to be a result of the increasing acid contents of the anolyte solutions. However, in two of the experiments the current density decreased appreciably during the last hour of operation (from 48 to 35 mA/cm^2 in Experiment 5723-120-1, and from 50 to 44 mA/cm^2 in Experiment 5723-119-3). It was thought that these decreases in current density might be caused by deposition of some



TYPICAL VARIATION OF COULOMB EFFICIENCY WITH TIME



TYPICAL VARIATION OF CURRENT DENSITY WITH TIME

Figure 7. Variations of Coulomb Efficiency and Current Density with Time

of the particles of iron hydroxide in the circulating catholyte solution upon the cation-exchange membrane or the cathode, which would increase the resistance of the cell. The cation-exchange membrane and the electrode were inspected after the cell was disassembled and black deposits were found on both. From the inspection it was difficult to tell whether the deposits were formed during the experiment or after the run was over. (The catholyte slurries were not filtered during the experiments and the solids contents increased throughout the runs. The slurries were filtered or allowed to settle after the runs were over.) Two additional experiments, described later, were performed in an attempt to determine whether deposition of iron hydroxide in the catholyte chamber caused increases of cell resistance.

The settling times of the slurries of precipitates formed in several of the experiments were determined. In these determinations, measured volumes of well-stirred slurries were placed in graduated cylinders and the positions of the line of demarcation between the clear liquid above the settling slurry and the slurry itself were recorded at timed intervals. The precipitates settled to 50% of the total volume in 30 minutes and to 25% of the volume in 60 minutes.

The coulomb efficiencies for acid production usually remained relatively high during the first 4 to 5 hr of each 6-hr run, but decreased somewhat during the last 1 or 2 hours of the run, as shown in Figure 7. When the concentration of acid in the anolyte solution exceeded about 45 g/l, the coulomb efficiencies began to decrease and in most of the experiments the acid concentration reached about 45 g/l in 4 to 5 hours.

As stated previously, in some of the experiments there were indications that particles of iron hydroxide in the circulating catholyte solution could have deposited on the cation exchange membrane facing the cathode of the three-compartment cell and caused an increase in the resistance of the cell.

The following experiments were performed to determine whether deposition of particles on the cation-exchange membrane or the cathode (or both) during operation contributed to the increases in cell resistance noted in some of the runs. A first acid-regeneration experiment (Experiment 5723-121-1) was performed in the usual

manner except that the rate of circulating the catholyte solution was decreased from the normal rate of about 30 ml/sec to about 10 ml/sec. A decreased rate of circulation should result in a lower rate of mixing within the cathode compartment, and, therefore, should increase the tendency of particles to deposit on surfaces in the cathode compartment. This first experiment was followed by an experiment (Experiment 5723-122-1) under identical conditions except that the circulation rate was increased to the usual 30 ml/sec.

The conditions used for these two experiments were: cell voltage = 4.5 V, temperature = 60°C, initial composition of anolyte solution = 3 g/l of H_2SO_4 and 21 g/l of $FeSO_4$, initial composition of solution circulated through center compartment = 25 g/l of H_2SO_4 and 93 g/l of $FeSO_4$, composition of catholyte solution = 1 N Na_2SO_4, the circulation rates of anolyte and center solution were about 30 ml/sec, and the circulation rate of the catholyte solution was about 10 ml/sec in one experiment and 30 ml/sec in the other.

A graph showing current density as a function of operating time for the two experiments is given in Figure 8. In the experiment performed with a low flow rate of circulating catholyte solution (Experiment 5723-121-1) the current density stayed at about 24 mA/cm^2 for slightly more than the first hour. It then decreased to about one-third of that value over the next 2 hours and remained at 8 to 9 mA/cm^2 during the final 3 hours of the experiment. In the experiment performed with a higher flow rate of catholyte solution, the current density was initially about 33 mA/cm^2 and increased slightly over the 6 hours of the experiment. On the basis of these two experiments it appeared that the flow rate of the catholyte solution will be important to the operation of the cell. The lower flow rate used in these two experiments apparently did not "scrub" deposited solids off of the surfaces in the catholyte compartments as thoroughly as the higher flow rate did.

In a full-scale acid-regeneration process, solids are not expected to build-up to as high a concentration in the circulating catholyte solution as they did in these experiments because in a full-scale process the solutions would be filtered continuously, whereas the solution was not filtered (or settled) until the end of the experiments.

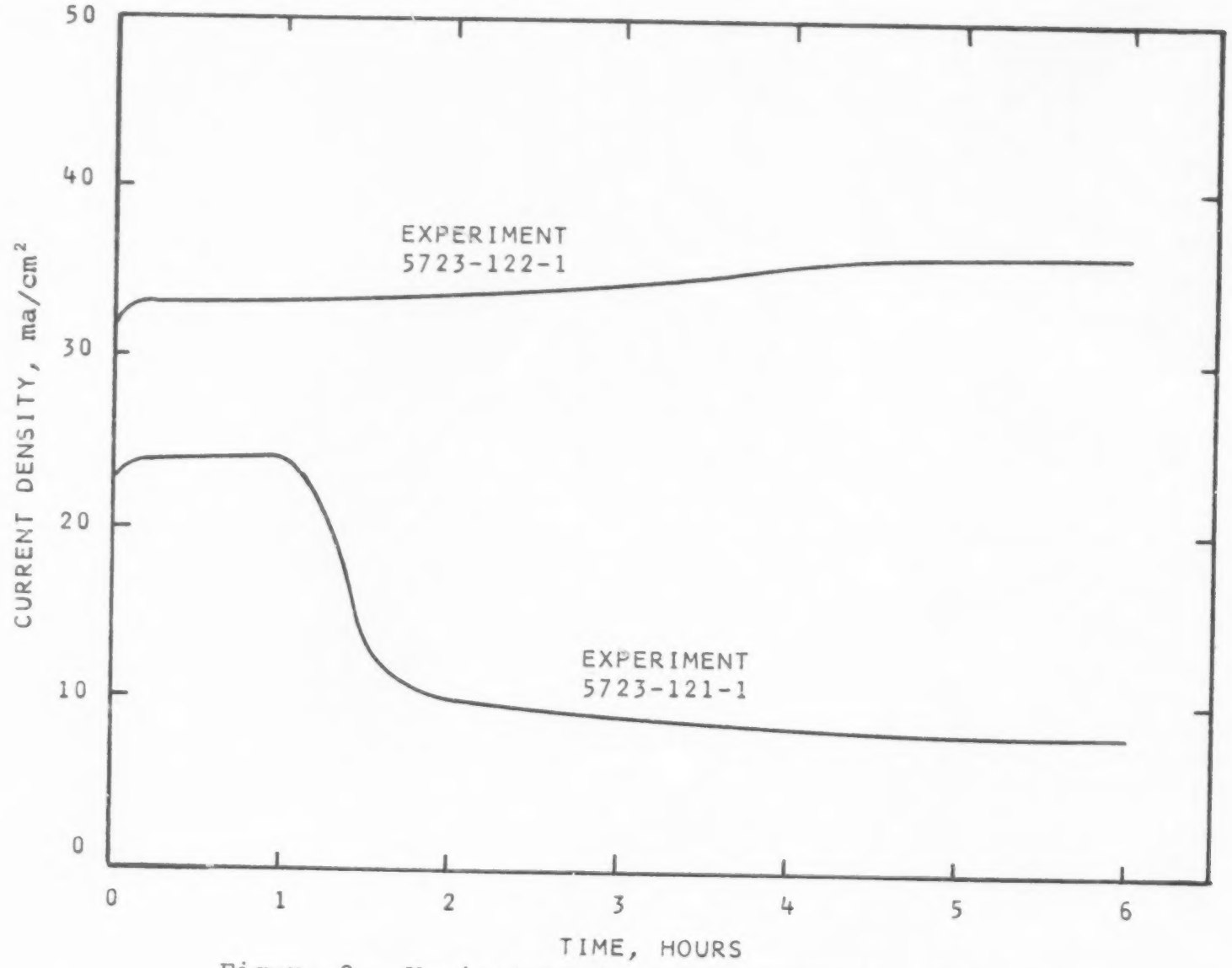


Figure 8. Variations in Current Density with Time

Nevertheless, the problem of solids build-up was considered to be serious and was studied further in the first experiments with actual pickle liquor.

(4) Experiments with actual pickle liquor

The results of the previous experiments performed with solutions of $FeSO_4$ and H_2SO_4 prepared in the laboratory afforded valuable information about the operation of the electromembrane cell in the batch-recycle regeneration process. However, it was desirable to determine whether the performance of the cell when treating actual spent pickle liquor would be different from that observed when the cell was used to treat the synthetic solutions. The organic pickling aids are one type of material that is known to be present in most actual spent pickle liquors that might be detrimental. Some organic material, such as humic acids, are known to foul ion-exchange membranes and cause their resistances to increase. If the resistances of membranes increase, the resulting energy costs for treating spent pickle liquor could be high.

A sample of spent liquor that contained an organic pickling aid (Activol made by the Henry Miller Company) was obtained from one of the industrial sponsors. The actual pickle liquor chosen was selected because its composition appeared to be typical of that of four of the six industrial sponsors. The composition of the sample used in the experiments, as determined by analyses, was:

	eq/l	g/l	wt %
H_2SO_4	0.61	30.0	2.8
$FeSO_4$	1.55	117.7	11.3
$Fe_2(SO_4)_3$	0.089	4.6	4.4

The specific gravity of the pickle liquor was 1.153.

In addition, an unknown amount of a proprietary organic pickling aid was known to be present. We did not have a method for analysis for the proprietary product, nor did we find out what materials were in it. However, the concentrations of the product normally used in pickling operations is about 1 g/l (0.1 wt %).

The three-compartment cell that was used in the experiments with synthetic solutions was used for the experiments with actual pickle liquor. The actual spent

pickle liquor (300 ml) was circulated through the center compartment of the cell, the same amount of a prepared solution that contained about 20 g/l of $FeSO_4$ and about 5 g/l of H_2SO_4 was circulated through the anolyte compartment, and the same amount of 1 N Na_2SO_4 solution was circulated through the catholyte compartment.

The first experiment with actual spent pickle liquor (5723-124-1, Figure 9) was performed to study further the possibility that precipitates of iron hydroxide would be deposited on surfaces in the catholyte compartment and cause an increase in the resistance of the cell.

This experiment was performed at 60°C with a cell voltage of 5 volts and the low flow rate of catholyte solution used previously (about 10 ml/sec). The membranes used in this experiment had been used in the two prior 6-hr experiments (5723-121-1 and 5723-122-1) with synthetic solutions to determine whether increases in cell resistances were a result of deposition of iron hydroxides on membrane or electrode surfaces in the catholyte compartment. After the prior experiments the membranes were stored 12 days; they were initially immersed in distilled water, but, because of evaporation, some areas of the membranes became dry.

During the course of Experiment 5723-124-1, several measures were tried in an attempt to gain more information about the effects of deposits of iron hydroxides on membrane and electrode surfaces on the resistance of the cell. From results of the previous experiments it seemed probable that deposits were formed on either the electrode or the membrane, or both. The deposits may have resulted from electrophoretic transport of the particles to the membrane or the electrode, or they may have resulted simply as a result of particles impinging against the surfaces as the slurry circulated through the compartment. If the particles were being transported electrophoretically and being held against the membrane or electrode as a result of the electric field, halting the electric current temporarily should permit some of the adherent particles to be stripped off of the surfaces by the action of the circulating solution, which should result in a reduction of cell resistance. Similarly, reversal of the electric current should be even more effective in reducing cell resistance. Accordingly, we tried both halting and reversing the

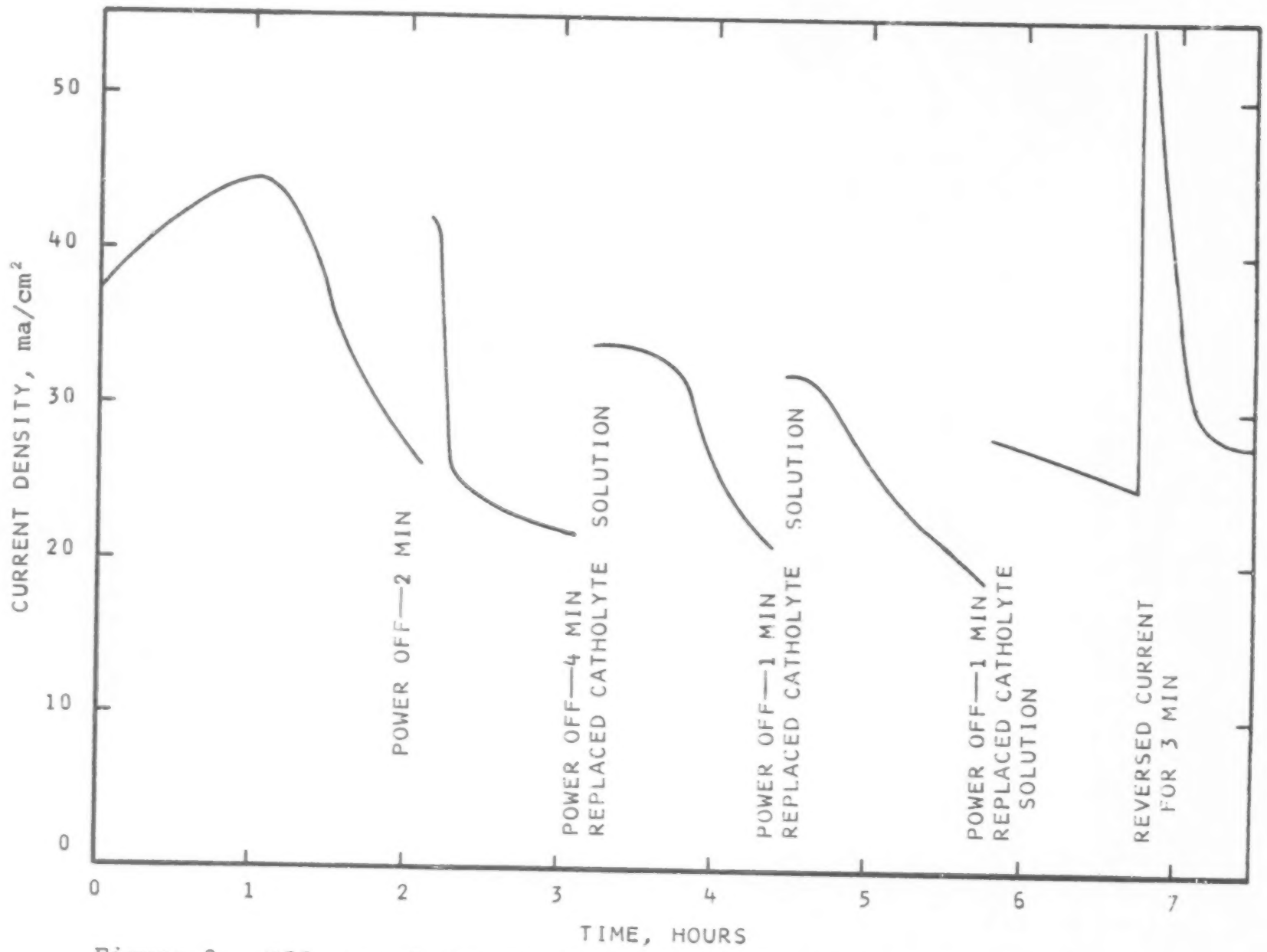


Figure 9. Effects of Changes in Operating Conditions on Current Density

electric current. We also tried replacing the catholyte solution, at least partially, with fresh solution after the solids content of the catholyte solution had increased to form a fairly concentrated slurry to see whether this would result in lower cell resistance. The results of these experiments are shown in Figure 9 as changes in current density (with a constant cell voltage) resulting from the changes in operating conditions.

During the first hour of operation the current density increased, probably as a result of the increasing acid content in the anolyte solution. After 2 hr and 8 min of operation the power was turned off for 2 min. When the power was turned back on, the current density was almost as high as it was after 1 hr of operation, but the current density dropped rapidly and the decrease in current density then continued at about the same rate as before the interruption of current. After a total of 3 hr and 8 min the power was turned off for 4 min and most of the catholyte solution (that in the reservoir) was replaced by fresh 1 N Na_2SO_4. When the power was turned on, the current increased from the previous 22 to 34 mA/cm^2. This increase was not as great as that at the previous interruption, but the current remained high for a longer period (almost 30 min). The replacement of catholyte solution was repeated after 4 hr and 20 min, and again after 5 hr and 40 min. After 6 hr and 45 min, the electrical current was reversed for 3 min and then returned to the original direction. The reversed current was 65 mA/cm^2. When the current was returned to the original direction, the current density was initially 52 mA/cm^2, but declined to 30 mA/cm^2 over a period of about 18 min. Over the last 24 min of the experiment the current density decreased to 27.5 mA/cm^2.

All of the above changes in current density as a result of changes in operating conditions indicated that the decreases in cell resistance that had been observed previously were partly, and perhaps largely, the result of deposition of iron hydroxides in the catholyte compartment—on the membrane, on the electrode, or on both. The results also suggested that replacement of the catholyte solution with clean 1 N Na_2SO_4 solution periodically in future experiments would come closer to simulating the operation to be expected in a plant operation, in which the catholyte solution would be continuously filtered so that the solids content would not build up.

The coulomb efficiency for acid production during Experiment 5723-124-1 was 65% compared with efficiencies of 60% and 49% for Experiments 5723-119-3 and -120-1 (see Table V) in which the cell voltage was also 5 volts but in which Fe_2SO_4-H_2SO_4 solutions were used instead of actual spent liquor. However, the coulomb efficiency for iron removal was only 25% in 5723-124-1 compared with efficiencies of 56 and 50% for the two experiments made with synthetic solutions. Because of these changes in coulomb efficiencies along with our knowledge that the membranes had partially dried during storage, it was thought that the transport properties of the membranes used for Experiment 5723-124-1 might have been altered by the partial drying or by accumulations of deposited iron hydroxide. Accordingly, we installed a new set of MC 3142 and MC 3148 membranes in the cell for two more experiments.

These two experiments were performed with the actual spent pickle liquor circulating through the center compartment of the three-compartment cell and with the same operating conditions as before except that the flow rates of the circulating solutions were approximately 30 ml/sec. In these experiments (Experiments 5723-125-1 and -125-2, Table V) the catholyte solution was replaced each hour with fresh 1 N Na_2SO_4 solution in an attempt to simulate a commercial operation in which the catholyte solution would be continuously filtered. In replacing the catholyte solution, the slurry of iron hydroxide was drained from the reservoir and an equal volume of 1 N Na_2SO_4 was added. Thus, the portion of the slurry that was in the tubing and the cell was not replaced; nevertheless, most of the solids were removed by the replacement procedure.

The average current density of 32 mA/cm^2 in the second experiment (5723-125-2) was lower than that in Experiment 5723-125-1 (41 mA/cm^2). At the end of Experiment 5723-125-1, the solutions were left in the cell overnight to keep the membranes moist. Just before Experiment 5723-125-2, the solutions were drained from the cell, the compartments were rinsed briefly with water, and filled with new solutions. There was some possibility that the overnight storage of the membranes in the presence of the iron hydroxide slurry in the catholyte compartment could have caused the lower current density.

Table V. Performance of Experimental Cell with Synthetic Solutions and with Actual Spent Pickle Liquor

Experiment 5723-	Cell voltage	Average current density, ma/cm^2	Average areal resistance of cell,[a] $ohm-cm^2$	Final H_2SO_4 concentration in anolyte		Average coulomb efficiencies, %		Comments
				g/l	Wt., %	For acid production[b]	For iron removal[c]	
With Fe_2SO_4-H_2SO_4 solutions								
119-2	4	24	62	32	3.1	70	71	New membranes
120-2	4	21	72	33	3.2	67	71	Membranes used 6 hours previously
122-1	4.5	36	56	50	4.9	61	50	New membranes
120-3	4.5	33	60	39	3.8	53	67	Membranes used 12 hours previously
119-3	5	45	56	59	5.7	60	56	New membranes
120-1	5	39	64	44	4.3	49	50	New membranes
119-4	6	50	70	57	5.6	52	44	New membranes
With actual spent pickle liquor								
125-1	5	41	60	66	6.4	61	60	New membranes
125-2	5	32	78	48	4.7	53	56	Membranes used 6 hours previously
127-1	5	47	53	60	5.8	66	72	New membranes
127-2	5	62	41	77	7.5	46	32	Membranes used 5 hours previously

a. Calculated as $R = \frac{E_{total} - E_{decomp.}}{i} = \frac{E_{total} - 2.5}{i}$, where E_{total} is the total voltage, $E_{decomp.}$ is the decomposition potential (2.5 volts), and i = current density, amp/cm^2.

b. Calculated from the difference between the total equivalents of H^+ ions at the start and end of the experiment in the solution circulated through the anolyte compartment.

c. Calculated from the difference between the total equivalents of iron ions at the start and end of the experiment in the solution circulated through the center compartment

Experiments 5723-127-1 and 5723-127-2 were performed with operating conditions identical to those in Experiment 5723-125-1 and -2 except that the flowrates of the solutions were increased to approximately 50 ml/sec. Experiment 5723-127-2 was performed as soon after Experiment 5723-127-1 as the three solutions could be drained and replaced.

In contrast to the two prior experiments, the average current density in Experiment 5723-127-2 was higher (62 ma/cm^2) than that in Experiment 5723-127-1 (47 mA/cm^2). Both current densities were higher than those observed in Experiments 5723-125-1 and -2, which suggests the more rapid circulation rates of the solutions in Experiments 5723-127-1 and -2 aided in reducing the resistance of the cell.

If the higher current density (62 mA/cm^2 at 60°C) could be maintained, the costs estimated later (Section VII) might be considerably reduced, since those estimates were based on average current densities of 48 to 54 ma/cm^2.

In Experiment 5723-127-2, there was a large decrease in the coulomb efficiency below that achieved in Experiment 5723-127-1. In contrast, the difference in coulomb efficiencies in Experiments 5723-125-1 and -2 was no greater than the difference in Experiments 5723-119-3 and 5723-120-1, which were performed with $FeSO_4$-H_2SO_4 solutions and with new membranes for each experiment.

After Experiment 5723-127-2 the cell was dismantled and the components were inspected. It was found that the membranes were in good physical condition, but the catholyte compartment contained heavy deposits of precipitate. It is not known whether the presence of this precipitate affected the coulomb efficiencies. A filter in the circulation loop for the catholyte solution would certainly have been desirable, but it would have caused pressure imbalances between the three compartments and attendant bowing or bending of the membranes without modifications of the apparatus. Limitations on time and money did not permit making those modifications and performing additional experiments.

The results of the experiments with actual pickle liquor indicate that the electromembrane cell was as satisfactory for treating actual spent pickle liquor as for treating the $FeSO_4$-H_2SO_4 solutions. However, some uncertainties remain concerning the effects of organic materials in actual spent pickle liquor in long-term operations. The trial with only one actual pickle liquor (and one type of organic pickling aid) does not provide an adequate basis for making a final conclusion regarding the suitability of the process for general plant use. In addition the performance of the cell should be evaluated over long periods of time before a final conclusion is made. We also believe a modified laboratory-scale apparatus with a filter in the catholyte-solution loop should be constructed and experiments with other actual pickle liquors should be made to obtain a broader base of data on which to base a decision on the technical feasibility of the process for plant operations.

VI. CONTINUOUS REGENERATION PROCESS

Some of the data from the batch-recycle experiments performed in the bench-scale equipment indicated it might be feasible to operate a continuous process for regenerating acid from spent pickle liquor. This process was not investigated experimentally because of limitations of time and money.

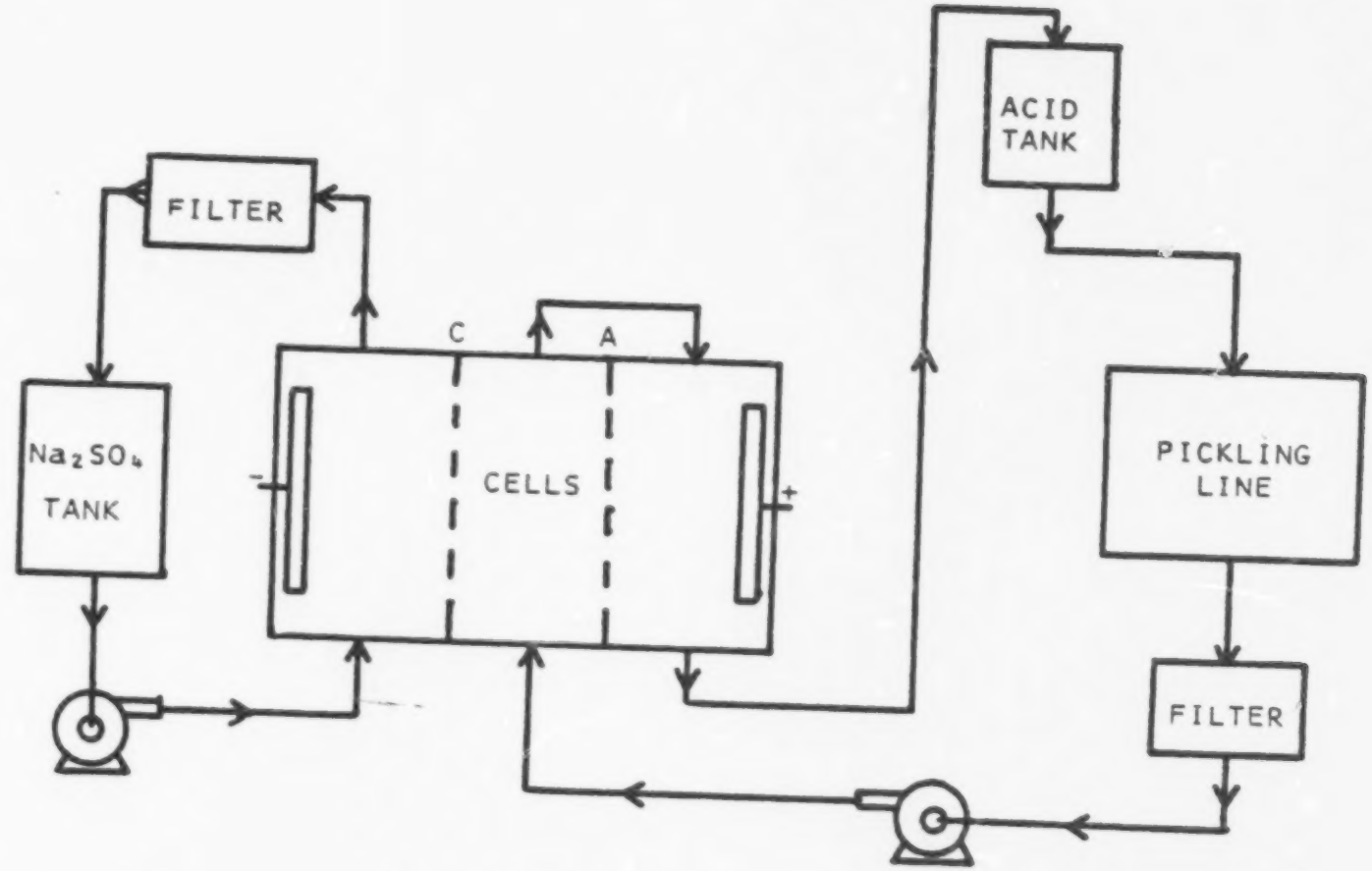
A flow diagram for the continuous acid-regeneration process is shown in Figure 10.

The pickling acid would contain enough free acid to assure adequate pickling, for example, 40 g/l., and a sufficiently low amount of $FeSO_4$ (e.g., 120 g/l.) so as not to impair the pickling action. In the continuous process, the liquor from the pickling line is circulated to the electromembrane cells and back to the pickling line. In the pickling line, the concentration of iron ions in the solution is increased; in the cells the iron ions added in the pickling line are removed and replaced by hydrogen ions to regenerate pickling acid. In the cells, the pickling solution flows first through the center compartments, where iron ions (along with some hydrogen ions) are transferred through the cation-exchange membranes into the catholyte compartments where iron ions combine with hydroxide ions to form insoluble iron hydroxides, which are filtered off. The pickling solution leaves the center compartments and enters the anolyte compartments where H^+ ions are formed to combine with SO_4^{-2} ions transferred through the anion-exchange membranes and regenerate H_2SO_4. The regenerated acid is sent back to the pickling line.

This continuous process is simpler and would require less equipment than the batch-recycle process.

Consideration of the electrolytic transfers that occur within the cells shows that:

- The coulomb efficiency for iron removal will be determined by the value of the transport number for iron ions in the cation-exchange membrane, t_c^{Fe}.



C - CATION-EXCHANGE MEMBRANE
A - ANION-EXCHANGE MEMBRANE

Figure 10. Flow Diagram of Continuous Regeneration Process

- The change in the hydrogen-ion concentration of the solution in the center compartments will be determined by the difference between t_a^H, which is the equivalents of H^+ ions per faraday entering the center compartment through the anion-exchange membrane, and t_c^H, which is the equivalents of H^+ ions per faraday leaving the center compartment through the cation-exchange membrane.

- The coulomb efficiency for enrichment of hydrogen ions in the anolyte compartment will be determined by the difference between the 1 equivalent per faraday of H^+ ions formed at the anode and the t_a^H equivalents of H^+ ions leaving through the anion-exchange membrane.

As a part of the determination of the feasibility of such a process, the specific permselectivity of cation-exchange membranes for H^+ ions relative to Fe^{+2} ions was calculated from the data obtained from the bench-scale experiments. The specific permselectivity of an ion-exchange membrane for one ion relative to another is defined as the ratio of the ionic velocities of the two ions in the membrane. Thus, the specific permselectivity of H^+ ions relative to Fe^{+2} ions can be calculated from the following equation:

$$T_{Fe^{+2}}^{H^+} = \frac{t^{H^+}}{C^{H^+}} \div \frac{t^{Fe^{+2}}}{C^{Fe^{+2}}} \qquad (1)$$

where: $T_{Fe^{+2}}^{H^+}$ = specific permselective of H^+ ions relative to Fe^{+2} ions

t^{H^+} = transport number of H^+ ions

$t^{Fe^{+2}}$ = transport number of Fe^{+2} ions

C^{H^+} = concentration of H^+ ions in the mixed solution, eq/l.

$C^{Fe^{+2}}$ = concentration of Fe^{+2} ions in the mixed solution, eq/l.

The transport numbers of H^+ and Fe^{+2} ions through the cation-exchange membranes were calculated from the data obtained in the batch-recycle experiments. The concentrations of H^+ and Fe^{+2} ions in the mixed solutions of H_2SO_4 and $FeSO_4$ that were circulated through the center compartment of the cell were also calculated. The specific permselectivities that were calculated from the transport numbers and concentrations ranged from values of 1.2 to 2.1, and the average value was 1.7. Because this appeared to be a fairly wide range we attempted to find relationships between the specific permselectivities and the concentrations of H^+ ions, the concentrations of Fe^{+2} ions, or the ratio of H^+ to Fe^{+2} in the solutions of H_2SO_4 and $FeSO_4$. However, there appeared to be little relationship between the above concentrations or ratios and the specific permselectivities. It appeared that the spread in the values of specific permselectivity was a result of slight inaccuracies inherent in the experiments used to determine the transport numbers. Since $t^{H^+} = 1 - t^{Fe^{+2}}$ the specific permselectivities calculated from Equation 1 would be sensitive to slight variations in the calculated values of t^{H^+} or $t^{Fe^{+2}}$ that might result from slight inaccuracies in experimental measurements. The specific permeability of H^+ to Fe^{+2} ions in MC 3142 membranes was taken to be 1.7 ± 0.4 and this value of specific permeability for H^+ to Fe^{+2} ions was used in the calculations of cost estimates for the continuous acid-regeneration process.

Data obtained in the bench-scale equipment while performing the batch-recycle experiments were also used to calculate the transport numbers of H^+ ions ($t_a^{H^+}$) through the MA 3148 anion-exchange membrane used in the cell for use in the determination of the feasibility of the continuous process of acid regeneration.

The fact that the coulomb efficiency for acid production decreased as the concentration of acid in the anolyte solution increased indicated that the transport of H^+ ions through the MA 3148 membrane increased and the transport of SO_4^{-2} ions decreased as the concentration of H_2SO_4 in the circulating anolyte solution increased during each 6-hr experiment. Therefore, we calculated values of $t_a^{H^+}$ from data for the changes in the concentration of H_2SO_4 in the anolyte solution during 1-hr

periods of operation during each experiment, since the concentration of H_2SO_4 increased with time during each experiment. In this way, we obtained an idea of the variation of $t_a^{H^+}$ with acid concentration.

Equation 2* was used for these calculations.

$$t_a^{H^+} = \frac{\Delta F - \Delta e}{\Delta F} \qquad (2)$$

where: $t_a^{H^+}$ = transport number of H^+ through the anion-exchange membrane

ΔF = faradays passed through the cell during a given time period

Δe = the change in the total equivalents of H_2SO_4 in the anolyte solution during the given time period

The variation of the calculated values of $t_a^{H^+}$ with the concentration of H_2SO_4 in the anolyte solution is shown in Figure 11. As indicated by the two lines, there were two groups of data points—one for cell voltages of 4 V and the other for cell voltages of 4.5 to 5 V. The reason for the separation of the two groups of points is not known; perhaps the difference is a result of some difference in concentration gradients in the boundary layers adjacent to the membrane surfaces.

In the calculations made as a part of the estimations of costs for the continuous process of acid regeneration (given later in Section VII), we used values of $t_a^{H^+}$ taken from the top line in Figure 10 because the assumption of high values of $t_a^{H^+}$ resulted in the highest and, therefore, most conservative estimations of operating costs.

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*Equation 2 stems from the fact that the increase in the total equivalents of H_2SO_4 in the anolyte solution equals the equivalents of SO_4^{-2} transferred through the anion-exchange membrane, and the equivalents of SO_4^{-2} transported divided by the faradays passed through the cell is $t_a^{SO_4^{-2}}$, and $t_a^{H^+} = 1 - t_a^{SO_4^{-2}}$.

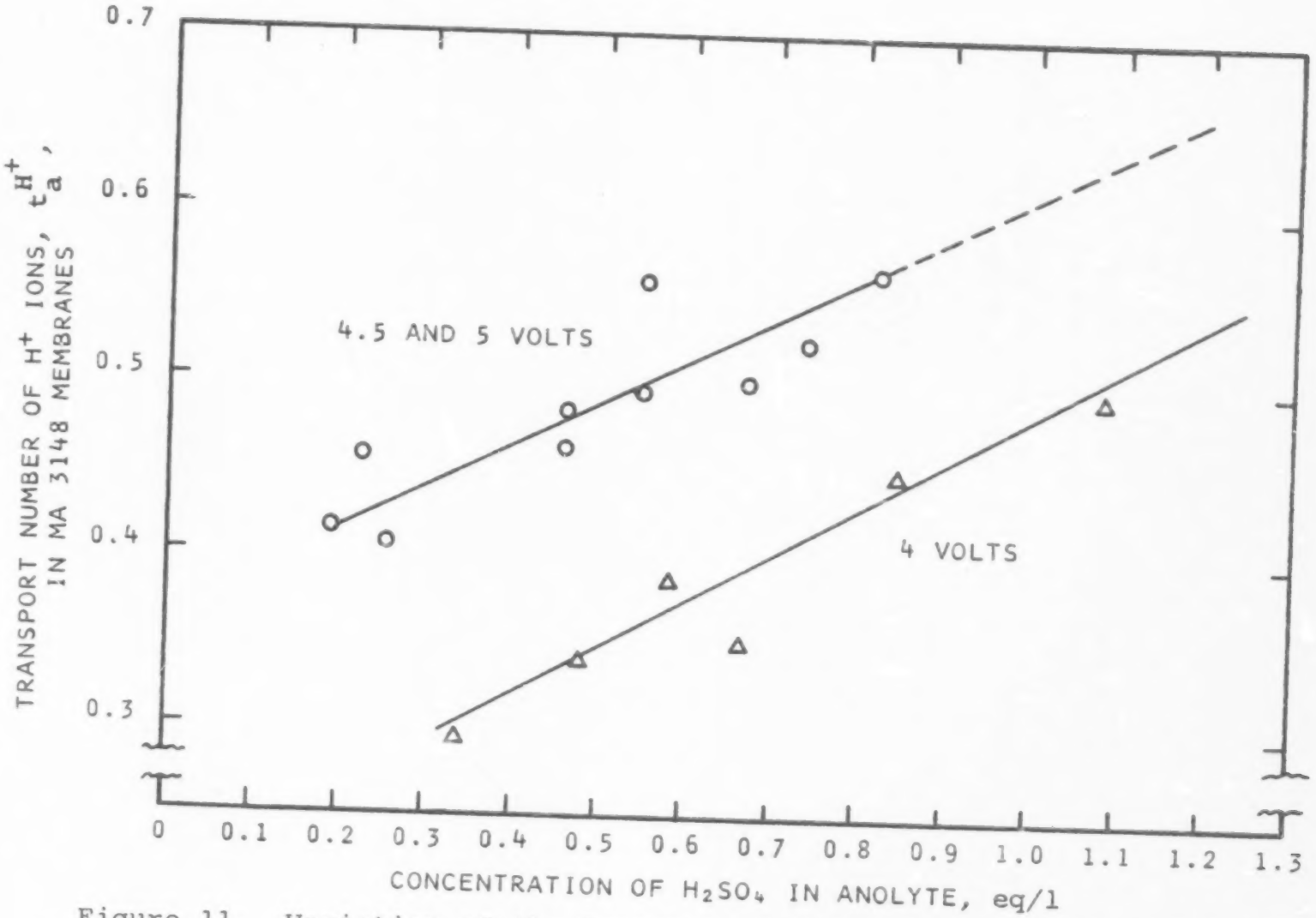

Figure 11. Variation of the Transport Number of H^+ Ions through MA 3148 Anion-Exchange Membrane with the Concentration of H_2SO_4 in the Anolyte Solution

We concluded that a continuous process for acid regeneration was feasible and for some pickling operations a continuous acid-regeneration process might be preferable to the batch-recycle type of processing.

VII. ESTIMATES OF COSTS

The capital and operating costs of the acid-regeneration process were estimated for pickling operations in which 2750 lb/day, 485 lb/day, and 44 lb/day of iron are dissolved in the pickling acid. The details of one of the cost estimates are given in the appendix to illustrate the methods used and the assumptions made.

These sizes of operation correspond approximately to the pickling operations of three of the industrial sponsors. The largest assumed scale of operation (2750 lb Fe/day) corresponds to a pickling operation that requires disposal of about 6700 gal. of spent liquor each day. The other two sizes (485 lb and 44 lb Fe/day) correspond to operations which require disposal of about 2400 and 200 gal./day of spent liquor, respectively. (The lack of correspondence between the ratios of pounds of iron dissolved to gallons of spent liquor for the three assumed sizes of plants illustrates the variations in pickling practice that result in wide variations in the concentrations of H_2SO_4 and $FeSO_4$ in the spent liquors.)

The assumptions pertaining to materials of construction for the cost estimates were based on the behavior of the materials used in the laboratory units during 80 hr of operation at 60°C. Some of the information about materials of construction is:

- The reinforced phenolic plastic from which the end frames and center frames of the cell were made (Micarta, grade 223, from Westinghouse Electric Corp.) showed no apparent degradation.

- Neither the graphite cathode nor the antimontial-lead anode (6% Sb, from National Lead Company) showed any signs of degradation.

- The Hastalloy pumps that were used gave satisfactory service except that the bearing packing on the pump that was used for the catholyte solution had to be replaced once. It is believed that this need for replacement was due largely to the solid particles in the catholyte solution, which would not be present in a large-scale process because that solution would be continuously filtered.

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- The room-temperature-vulcanizing silicone rubber (Silastic 731 RTV, Dow Corning Corp.) used to form gasketing surfaces on the end frames and center frames gave satisfactory service.

It appears that the materials used for the components of the cell and in the pump should give satisfactory service in large units. However, longer runs in a pilot-plant cell will be needed to provide more meaningful data on service lifetimes of materials.

The capital costs and operating costs for the 2750 lb Fe/day operation are compared in Tables VI and VII for three variations of processing: batch-recycle with 4.5 V/unit cell, batch-recycle with 5 V/unit cell, and continuous processing with 5 V/unit cell.

Table VI shows that the capital needed for the batch-recycle process will be slightly less when 5 V/unit cell is used than when 4 V/unit cell is used because of the lower cost of the cells. Table VII shows that the operating cost also will be lower with 5 V/unit cell. The data in these tables also show that both the capital needed and the operating costs will be less for the continuous process than for the batch-recycle process.

The capital costs for a plant to remove 485 lb of dissolved iron per day and regenerate the acid by the continuous process were estimated to be $66,900. The operating costs with 5 V/unit cell are shown in Table VIII.

The capital costs for a plant to remove 44 lb of dissolved iron per day and regenerate the acid by the continuous process were estimated to be $12,200. The operating costs with 5 V/unit cell to remove 44 lb Fe/day are shown in Table IX.

The daily operating costs for removal of 485 lb Fe/day were not as much below those for removal of 2740 lb Fe/day as might be expected. The main reason is that the estimated cost of operating and maintenance labor did not decrease at all.

Table VI. Capital Costs for Electromembrane Acid-Regeneration Processes for Treating Spent Pickle Liquor (Size—2750 Pounds of Iron Dissolved per Day)

Item	Capital costs, Batch-recycle with 4.5 volts/cell	Batch-recycle with 5 volts/cell	Continuous process with 5 volts/cell
Cells	45,500	38,800	38,800
Rectifiers	33,200	37,000	37,000
Tanks	6,360	6,360	3,180
Pumps	1,160	1,160	720
Filters	7,200	7,200	7,200
Heat exchanger	1,900	1,900	1,900
Voltmeter	300	300	300
Ammeter	300	300	300
Timer and solenoid valves (or other instruments)	1,450	1,450	1,450
	$97,370	$94,470	$90,850
Cost of installation[a]	4,800	4,800	3,900
Installed cost of principle items of equipment	$102,170	$99,270	$94,750
Cost of piping and wiring[b]	61,300	59,500	56,600
Sub-total I	$163,470	$158,770	$151,350
Other costs of construction[c]	81,700	79,000	75,650
Total cost	$245,170	$237,770	$217,000

a. It is assumed the equipment can be housed in an existing building and that no additional foundations, supports, vents, or chutes will be needed (see appendix).

b. 60% of principal items of equipment.

c. 50% of sub-total 1. Includes costs of providing utility services (electrical, steam, etc.), site preparation, interest on funds for construction, contractor's profit, and contingencies.

Table VII. Total Costs for Electromembrane Acid-Regeneration Processes for Treating Spent Pickle Liquor (Size—2750 Pounds of Iron Dissolved per Day)

Conditions

In batch-recycle process:
- Composition of spent pickle liquor:
  - H_2SO_4 - 25 g/l (0.51N) 2.3 wt. %
  - $FeSO_4$ - 74 g/l (0.97N) 6.7 wt. %
- Composition of regenerated acid:
  - H_2SO_4 - 60 g/l (1.225N) 5.7 wt. %
  - $FeSO_4$ - 20 g/l (0.26N) 1.9 wt. %
- Time of cycle - 6 hr
- Temperature - 70°C
- Coulomb efficiency - 50%

In continuous process:
- Average composition of pickle liquor:
  - H_2SO_4 - 40 g/l (0.815N) 3.6 wt. %
  - $FeSO_4$ - 120 g/l (1.600N) 10.5 wt. %
- Temperature - 70°C
- Coulomb efficiency - 50%[a]

Item	Total costs, $/day					
	Batch-recycle with 4.5 volts/cell		Batch-recycle with 5 volts/cell		Continuous process with 5 volts/cell	
Make-up acid	3.50		3.50		3.50	
Energy	94.58		104.88		104.88	
Operating labor	24.00		24.00		24.00	
Maintenance labor	8.00		8.00		8.00	
Supervision	3.20		3.20		3.20	
Payroll extras	7.06		7.06		7.06	
Operating supplies	8.20		7.24		7.24	
Membrane replacement	28.80		21.80		21.80	
Electrode replacement	3.78		3.22		3.22	
General overhead	4.80		4.80		4.80	
Taxes and insurance	8.20		7.24		7.24	
Interest on working capital	6.67		6.67		6.67	
Total direct costs	201.92		198.61		198.61	
Amortization:						
at 8% - 15 yr	95.00		92.00		84.50	
at 10% - 15 yr		108.00		104.00		98.50
Total costs	$296.92	$309.92	$290.61	$302.61	$283.11	$297.11
Total costs on the basis of $/equivalent gallon of spent liquor[b]	$0.0443	$0.0462	$0.0435	$0.0451	$0.0420	$0.0442

a. Calculations show the coulomb efficiency will be 50% when the pickling acid contains 0.815 eq/l of H_2SO_4 and 1.60 eq/l of $FeSO_4$ and the specific permselectivity is 1.7.

b. Estimated daily operating costs divided by the gallons of spent liquor being disposed of in the existing process.

Table VIII. Total Costs for an Electromembrane Acid-Regeneration Process
(Continuous process assumed with 5 volts/cell)
(Size—485 Pounds of Iron Dissolved per Day)

Conditions

Average composition of pickling solution:[a]
H_2SO_4 - 40 g/l (0.815N) 3.6 wt %
$FeSO_4$ - 120 g/l (1.600N) 10.5 wt %

Spacings between membranes (or membranes and electrodes) - 0.4 cm
Temperature - 70°C
Coulomb efficiency - 50%[a]

Item	Cost, $/day	
Make-up acid	0.80	
Energy	21.60	
Operating labor	24.00	
Maintenance labor	8.00	
Supervision	3.20	
Payroll extras	7.06	
Operating supplies	2.23	
Membrane replacement	3.90	
Electrode replacement	0.57	
General overhead	4.80	
Taxes and insurance	2.23	
Total direct costs	78.39	
Amortization:		
at 8% - 15 yr	26.00	
at 10% - 15 yr		30.40
Total cost	$104.39	$108.79

Operating costs on the basis of $/equivalent gallon of spent liquor

With amortization:
at 8% - 15 yr $0.0435/gal. of spent pickle liquor
at 10% - 15 yr $0.0455/gal. of spent pickle liquor

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a. Calculations show the coulomb efficiency will be 50% when the pickling acid contains 0.815 eq/l of H_2SO_4 and 1.60 eq/l of $FeSO_4$ and the specific permselectivity is 1.7.

Table IX. Operating Costs for an
Electromembrane Acid-Regeneration Process
(Continuous process assumed with 5 volts/cell)
(Size - 44 pounds of iron dissolved/day)

Conditions

Average composition of pickling solution:[a]
H_2SO_4 - 40 g/l (0.815N) 3.6 wt %
$FeSO_4$ - 120 g/l (1.600N) 10.5 wt %

Spacings between membranes (or membranes and electrodes) - 0.4 cm
Temperature - 70°C
Coulomb efficiency - 50%[a]

Item		Cost, $/day
Make-up acid		0.14
Energy		2.94
Operating labor		24.00
Maintenance labor		8.00
Supervision		3.20
Payroll extras		7.04
Operating supplies		0.27
Membrane replacement		0.42
Electrode replacement		0.06
General overhead		0.53
Taxes and insurance		0.27
Total direct costs		46.87
Amortization:		
at 8% - 15 yr	7.48	
at 10% - 15 yr		8.70
	$54.35	$55.57

a. Calculations show the coulomb efficiency will be 50% when the pickling acid contains 0.815 eq/l of H_2SO_4 and 1.60 eq/l of $FeSO_4$ and the specific permselectivity is 1.7.

For the small plant for removal of 44 lb Fe/day, the estimated capital costs are much higher per unit of throughput ($96/daily gal. of spent liquor) than for the larger plants $28 and $33/daily gal.). This was expected because the smaller processing equipment often costs nearly as much as larger sizes. The costs for operating labor, maintenance labor, supervision and payroll extras ($32.24 total) are by far the major costs for this scale of operation. It may be possible to assign an existing operator (with some other major task) to make the routine checks of instruments and thus reduce the costs indicated in Table IX appreciably.

The estimated operating costs should be considered in relation to the increasing problems of disposal and to the present costs of purchasing acid and disposing of spent pickle liquor, which range from about $0.015/gal. to $0.06/gal., as indicated below.

Disposal method	Cost of disposal, $/gal.	Cost of acid, $/gal.	Total cost, $/gal.
Deep-well injection	0.005 to 0.01	0.01 to 0.02	0.015 to 0.03
Neutralizing and lagooning	0.01 to 0.02	0.01 to 0.02	0.02 to 0.04
Neutralizing and land-fill	0.02 to 0.03	0.01 to 0.02	0.03 to 0.05
Hauling	0.02 to 0.04	0.01 to 0.02	0.03 to 0.06

The cheaper methods of disposal (deep-well injection and neutralizing and lagooning) cannot be used at all localities without additional costs for transporting the spent liquor.

The estimated costs for the large and intermediate sizes of treatment plants are in the range of costs for the hauling and neutralization and land-fill. Therefore, the estimated costs suggest that the electromembrane process will be competitive in cost with the present

operations. In addition, if the electromembrane process is used, it will be necessary to dispose only of the solid hydroxides of iron. Disposal of these insoluble solids can be achieved by earth-fill methods with no problems of water or air pollution. Thus, the proposed electromembrane process should eliminate the pressures to find methods of disposal that will not result in pollution problems.

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APPENDIX

Cost Estimates

Estimates of capital and operating costs for the acid-regeneration process have been prepared for three sizes of pickling operation, for two variations in type of processing (batch and continuous), and for two assumed cell voltages. The details of one of the cost estimates are given below to illustrate the estimating methods used.

For this estimate, we assumed the batch-recycle method of operation described in Section III would be used. We assumed that the unit to treat spent pickle liquor would be required to remove approximately 2750 lb Fe/day from the liquor, which is roughly the amount of iron that one of the industrial sponsors now accumulates in the pickling bath each day. (This sponsor now must dispose of about 6700 gal./day of spent pickle liquor.) Other assumptions were as follows:

- The unit will be operated 24 hr/day and 300 days/yr.
- Unit cells of the type shown in Figure 5 will be used with spacings of 0.4 cm between membranes and electrodes, or between membranes for all three compartments. Many three-compartment unit cells will be assembled into a filter-press type of stack like those used for production of hydrogen and oxygen to conserve floor space.
- Bipolar electrodes will be used in the filter-press cells. They will be low carbon steel on the surfaces used as cathodes and antimonial lead on the surfaces used as anodes.
- The operating temperatures will be 70°C.
- The cell voltage will be 4.5 V/unit cell.
- The coulomb efficiency will be 50%. For cell voltages of 4.5 V, coulomb efficiencies from 50% to 56% were achieved in the experiments.
- The efficiency of rectification will be 94%.

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- The cost of energy will be $0.008/kwh. This is higher than the national average of $0.007/kwh.

- The cost of membranes will be $3.00/ft^2.

- The percentage of the membranes utilized will be 85%.

- Average membrane lifetime will be 2 yr.

- Average electrode lifetime will be 6 yr.

- The cost of bipolar electrodes will be $2.65/ft^2 (based on cost of $1.98/ft^2 for lead, $0.42/ft^2 for steel, and $0.25/ft^2 for fabrication). The electrodes consist of a 1/16-in. thickness of antimonial lead rolled onto 16-gage steel.

- Rectifiers will cost $70 per kw of capacity.

- The average current density will be 48 mA/cm^2, or 44.5 A/ft^2 (based on our experimental data).

- Six hours per day of an operator's time will be needed.

- Two hours per day of a maintenance man's time will be needed.

- Supervision will be 10% of direct labor.

- The operator and maintenance man will receive $4.00/hr.

- Payroll extras will be 20% of direct labor costs.

- Cost of operating supplies will be 1% of capital investment.

- General administrative overhead will be 15% of direct labor cost.

- Capital investment will be depreciated over the 15 years estimated as the lifetime of the plant. The capital investment includes the cost of all components, except the membranes and electrodes which are treated as expendable items and costs for their replacement are included in addition to the amortization of capital costs.

- The interest to be paid for the money needed for the capital investment was calculated for two rates—8% and 10%. Since this investment will almost certainly not be made until 1972, it is difficult to foresee what an appropriate rate of return would be at that time. Therefore, the cost of amortization is given on two bases.

- Taxes and insurance will be 1% of the total investment.

The costs of standard items of equipment, such as tanks, pumps, and filters, were estimated by updating information given by H. E. Mills.[5]

The general method of estimating capital costs was that described by C. Miller.[6] In this method of estimation, the installed cost of the principal items of equipment is adjusted by certain factors to obtain an estimate of the total capital cost.

The total area of unit cells that will be needed to remove 2750 lb Fe/day (i.e., 0.516 g eq/sec) with a coulomb efficiency of 50% was estimated as follows:

$$0.516 \text{ g eq/sec} \times 96{,}500 \text{ coul/g eq} \times (1/0.5) = 99{,}500 \text{ coul/sec}$$

$$99{,}500 \text{ A} \div 44.5 \text{ A/ft}^2 = 2240 \text{ ft}^2$$

A design of unit cells was selected in which the membranes and electrodes will be 39.4 in. square. With a total area of 10.8 ft^2/cell and an effective area of 9.4 ft^2, the number of unit cells needed will be $2240 \div 9.4 = 238$. A unit cell consists of a cathode, an anode, an anion-exchange membrane, a cation-exchange membrane and the

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5. H. E. Mills, "Costs of Process Equipment", in Modern Cost-Engineering Techniques, H. Popper, Editor, McGraw-Hill Book Company, New York (1970).

6. C. Miller, "New Cost Factors Give Quick, Accurate Estimates", in Modern Cost-Engineering Techniques, H Popper, Editor, McGraw-Hill Book Company, New York (1970).

three mesh-like spacers needed to maintain the proper spacing between membranes and electrodes. Each unit cell will require three cell frames and spacers, one anion-exchange membrane, one cation-exchange membrane, and one bipolar electrode. The cost of the 238 unit cells complete with end frames and clamping bolts is as follows:

Cell frames—238 x 3 x \$25/frame =	\$17,900
Ion-exchange membranes— 238 x 2 x \$3/ft^2 x 10.8 ft^2 =	15,500
Electrodes—238 x \$2.65/ft^2 x 10.8 ft^2 =	6,800
End frames and bolts	1,250
Assembly cost and contingency (10% of above items)	4,150
	\$45,500

The cost of the rectifiers was estimated as follows:

99,500 A x 4.5 V = 447,000 V A d-c or 447,000 ÷ 0.94 = 475,000 W or 475 kw.

Cost of rectifiers = 475 x \$70/kw = \$33,250.

Four 4000-gal. Fiberglas-reinforced tanks will be needed. In Owens-Corning Corporation Catalog, Type 104MC2 tanks (4000 gal.) sell for \$1590 each. The freight cost will just about offset the 10% discount that was quoted. The cost of four tanks will be 4 x \$1590 = \$6360.

Four pumps will be needed. Eastern Manufacturing Company's Model D-11 pumps with Hastalloy impellers and cases should be satisfactory. These pumps sell for \$290 each, so the cost will be 4 x \$290 = \$1160.

One sand filter will be needed to filter particulate matter from the spent pickle liquor. The cost was estimated to be \$1200.

The continuous pressure filters needed for the filtration of the precipitated iron hydroxides were estimated to cost \$6000, if made of 316 stainless steel. Two quick-opening, vertical-leaf pressure filters (each with 130 square feet of filtering area will be needed. One filter will be on-stream while the cake is being dumped from the other.

The heat exchanger needed in the pickling line to eliminate the need for heating with direct steam is estimated to cost $1900.

The instruments needed (a voltmeter, ammeter, and timer with solenoid valves) are estimated to cost $2050.

Table X summarizes the costs of the principal items of equipment and the other costs comprising the estimated total costs.

The operating costs were then estimated.

	Cost, $/day
The cost of energy was estimated to be	
d-c energy = 475 kwh/hr x 24 hr/day x $0.008/kwh	91.50
a-c energy (for pumps, and filter) 16 kwh/hr x 24 x $0.008/kwh	3.08
Total	94.58
The cost of operating labor = 6 hr x $4.00/hr	24.00
The cost of maintenance labor = 2 hr x $4.00/hr	8.00
The cost of supervision, 10% of direct labor, 10% x $32.00	3.20
The cost of payroll extras, 20% of total labor, 20% x $35.20	7.06
The cost of operating supplies 1% of $245,170 for 300 days (1 yr)	8.20
The cost of membrane replacement $15,500 for 600 days (2 yr)	25.80
The cost of electrode replacement $6,800 for 1800 days (6 yr)	3.78
The cost of general overhead, 15% of direct labor, 15% of $32.00	4.80
The cost of taxes and insurance, 1% of capital cost, 1% of $245,170 for 300 days (1 yr)	8.20
The cost of interest on working capital 10% of $20,000 for 300 days (1 yr)	6.67

The operating costs are summarized in Table XI.

Table X. Estimated Capital Costs for Acid-Regeneration Process (For pickling operation that dissolves 2750 lb Fe/day)

Item	Cost, $	Estimated hours to install[a]
Cells	45,500	120
Rectifiers	33,200	80
Tanks	6,360	120
Pumps	1,160	60
Filters	7,200	50
Heat exchanger	1,900	20
Voltmeter	300	5
Ammeter	300	5
Timer and solenoid valves	1,450	20
	97,370	480
Installation[b] ($10/hr x 480)	4,800	
Installed cost of principal items of equipment (PIE)	102,170	
Piping and wiring (60% of PIE)	61,300	
Sub-total	163,470	
Other construction costs[c] (50% of sub-total	81,700	
Total cost	245,170	

Amortization: at 8% for 15 yr = 0.117 ($245,170) = $28,600
at 10% for 15 yr = 0.132 ($245,170) = $32,400

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a. Estimated installation times from reference 6.

b. It is assumed that no additional building, foundations, or vents will be needed.

c. Includes the costs of providing utility services, site preparation, interest on construction funds, and contingency.

Table XI. Operating Costs for Electromembrane Acid-Regeneration Process

Item	Cost,$/day	
Acid (250 lb/day make-up at $0.014/lb)	3.50	
Energy	94.58	
Operating labor	24.00	
Maintenance labor	8.00	
Supervision	3.20	
Payroll extras	7.06	
Operating supplies	8.20	
Membrane replacement	28.80	
Electrode replacement	3.78	
General overhead	4.80	
Taxes and insurance	8.20	
Interest on working capital	6.67	
	201.92	
Amortization: at 8% = $28,600/300	95.00	
at 10% = $32,400/300		108.00
Daily operating cost: amortized at 8%	296.92	
amortized at 10%		309.92

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10 Author(s)

Robert E. Lacey

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27 Abstract Studies of an electromembrane process for regenerating acid from spent sulfuric acid pickle liquor have indicated that the process is technically feasible. The studies have shown that the iron ions in spent pickle liquor can be removed and replaced by hydrogen ions to regenerate H_2SO_4 in electromembrane cells.

A method of removing iron from spent liquor that involves the formation of insoluble iron hydroxides is preferrable to plating iron metal onto cathodes.

Estimated treatment costs were $0.045 ± 0.002 per gallon, whereas the combined costs of purchasing acid and disposing of spent liquor by existing methods were in the range of $0.015 to $0.06 per gallon of spent liquor.

A determination of the long-term performance of the ion-exchange membranes when treating actual pickle liquors that contain organic pickling aids is needed.

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Abstractor Robert E. Lacey | Institution Southern Research Institute, Birmingham, Alabama

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